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DEVELOPMENT DOCUMENT FOR EFFLUENT LIMITATIONS GUIDELINES AND NEW SOURCE PERFORMANCE STANDARDS FOR THE MAJOR INORGANIC PRODUCTS SEGMENT OF THE INORGANIC CHEMICALS MANUFACTURING POINT SOURCE CATEGORY

ENVIRONMENTAL PROTECTION AGENCY

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Effluent limitations guidelines contained herein set forth the degree of effluent reduction attainable through the application of the best practicable control technology currently available and the degree of effluent reduction attainable through the application of the best available technology economically achievable which must be achieved by existing point sources by July 1, 1977 and July 1, 1983, respectively. The standards of performance and pretreatment standards for new sources contained herein set forth the degree of effluent reduction which is achievable through the application of the best available demonstrated control technology, processes, operating methods, or other alternatives

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for

EFFLUENT LIMITATIONS GUIDELINES

and

NEW SOURCE PERFORMANCE STANDARDS

for the

MAJOR INORGANIC PRODUCTS SEGMENT OF THE INORGANIC CHEMICALS MANUFACTURING POINT SOURCE CATEGORY

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ABSTRACT

This document presents the findings of an extensive study of major inorganic chemicals manufacture for the purpose of developing effluent limitation guidelines for existing point sources and standards of performance and pretreatment standards for new sources to implement Sections 304, 306 and 307 of the Federal Water Pollution Control Act, as amended (33 U.S.C. 1551, 1314, and 1316, 86 Stat. 816 et. seq.) (the "Act").

Effluent limitations guidelines contained herein set forth the degree of effluent reduction attainable through the application of the best practicable control technology currently available and the degree of effluent reduction attainable through the application of the best available technology economically achievable which must be achieved by existing point sources by July 1, 1977 and July 1, 1983, respectively. The standards of performance and pretreatment standards for new sources contained herein set forth the degree of effluent reduction which is achievable through the application of the best available demonstrated control technology, processes, operating methods, or other alternatives.

Based on the application of best practicable technology currently available 12 of the 22 chemicals under study can be manufactured with no discharge of process waste water pollutants to navigable waters. With the best available technology economically achievable 20 chemicals can be manufactured with no discharge of process waste water pollutants to navigable waters. No discharge of process waste water pollutants to navigable waters is required as a new source performance standard for all chemicals except titanium dioxide, chlorine, sodium dichromate, sodium sulfite and sodium chloride.

Supporting data and rationale for development of the effluent limitations guidelines and standards of performance are contained in this report.

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SECTION I

CONCLUSIONS

For the purpose of establishing effluent limitation guidelines and standards of performance, the major inorganic products segment of the inorganic chemicals manufacturing point source category was divided into 22 product subcategories consistent with the chemical produced. In some cases, the product subcategory was further subdivided to reflect different manufacturing processes used to produce the same chemical. This method of categorization reflects differences in the nature of raw wastes generated in the manufacture of different chemicals, as well as its treatability. Factors such as plant age, plant size and geographical location did not justify further segmentation of the industry.

Based on best practicable control technology currently available (BPCTCA), 12 of the 22 chemicals under study can be manufactured with no discharge of process waste water pollutants to navigable waters. With the application of best available technology economically achievable (BATEA), 20 of the 22 chemicals can be manufactured with no discharge of process waste water pollutants to navigable waters. No discharge of process waste water pollutants to navigable waters is, also, achievable as a new source performance standard (NSPS) based on the best demonstrated control technologies, processes, operating methods or other alternatives (BDCT) for all chemicals except titanium dioxide, chlorine, sodium dichromate, sodium sulfite, and sodium chloride.

This study included 22 of the major inorganic chemicals of SIC categories 2812, 2816, and 2819 which discharge significant quantities of process waste water pollutants into the navigable waters of the United States. A forthcoming study includes certain other inorganic chemicals and industrial gases whose annual U.S. production volume exceeds 450 kkg (500 ton) with significant waste discharge potential.

SECTION II

RECOMMENDATIONS

The effluent limitation guidelines representing the effluent reduction attainable by the application of best practicable control technology currently available and the effluent reduction attainable by the application of best available technology economically achievable are shown in Table 1. Also shown are the new source performance standards for each chemical subcategory.

The figures in the table represent the thirty-day average allowable discharge. In all cases the daily maximum is twice the thirty-day average. All process waste water discharges must be within the pH range of 6.0 - 9.0. Effluent limitation guidelines for non-contact cooling water and waste streams resulting from steam and water supply are being developed in a separate study.

The technologies on which such guidelines are based are discussed in detail in Sections III - XI, along with the rationale for selecting the various levels of technology.

Table 1. EFFLUENT LIMITATION GUIDELINES

AND NEW SOURCE PERFORMANCE STANDARDS

Product Subcategory	Limitation based on BPCTCA (kg/kkg)	Limitation based on BATEA (kg/kkg)	New Source Performance Standard (kg/kkg)
Aluminum Chloride	no discharge of pwwp*	no discharge of pwwp	no discharge of pwwp
Aluminum Sulfate	no discharge of pwwp	no discharge of pwwp	no discharge of pwwp
Calcium Carbide	no discharge of pwwp	no discharge of pwwp	no discharge of pwwp
Calcium Chloride	TSS 0.0082	no discharge of pwwp	no discharge of pwwp
Calcium Oxide and Hydroxide	no discharge of pwwp	no discharge of pwwp	no discharge of pwwp
Chlorine			
a) mercury cell process	TSS 0.32 Mercury 0.00014	no discharge of pwwp	TSS 0.22 Mercury 0.00007
b) diaphragm cell process	TSS 0.32 Lead 0.0025	no discharge of pwwp	TSS 0.22 Lead detectable limit
Hydrochloric Acid	no discharge of pwwp	no discharge of pwwp	no discharge of pwwp
Hydrofluoric Acid	no discharge of pwwp	no discharge of pwwp	no discharge of pwwp
Hydrogen Peroxide			
a) organic process	TSS 0.4 TOC 0.22	no discharge of pwwp	no discharge of pwwp
b) electrolytic process	TSS 0.0025 Cyanide 0.0002		
Nitric Acid	no discharge of pwwp.	no discharge of pwwp	no discharge of pwwp
Potassium Metal	no discharge of pwwp	no discharge of pwwp	no discharge of pwwp
Potassium Dichromate	no discharge of pwwp	no discharge of pwwp	no discharge of pwwp
Potassium Sulfate	no discharge of pwwp	no discharge of pwwp	no discharge of pwwp
Sodium Bicarbonate	no discharge of pwwp	no discharge of pwwp	no discharge of pwwp
Sodium Carbonate	TSS 0.17	TSS 0.10	no discharge of pwwp
Sodium Chloride			
a) solar evaporation process	uncontaminated waste bitterns may be returned to the source	same as BPCTCA	same as BPCTCA
b) solution brine-mining process	TSS 0.17	no discharge of pwwp	no discharge of pwwp
Sodium Dichromate	TSS 0.22 Cr(T) 0.0044 Cr(+6) 0.0005	no discharge of pwwp	TSS 0.15 Cr(T) 0.0044 Cr(+6) 0.0005
Sodium Metal	TSS 0.23	no discharge of pwwp	no discharge of pwwp
Sodium Silicate	TSS 0.005	no discharge of pwwp	no discharge of pwwp
Sodium Sulfite	TSS 0.016 COD 1.7 (as Cr_2O_7)	no discharge of pwwp no discharge of pwwp	TSS 0.016 COD 1.7 (as Cr_2O_7)
Sulfuric Acid	no discharge of pwwp	no discharge of pwwp	no discharge of pwwp
Titanium Dioxide			
a) chloride process	TSS 2.3 Iron 0.36	TSS 1.3 Iron 0.18	TSS 1.3 Iron 0.18
b) sulfate process	TSS 10.5 Iron 0.84	TSS 5.3 Iron 0.42	TSS 5.3 Iron 0.42

*process waste water pollutants

INTRODUCTION

PURPOSE AND AUTHORITY

The United States Environmental Protection Agency (EPA) is charged under the Federal Water Pollution Control Act Amendments of 1972 with establishing effluent limitations which must be achieved by point sources of discharge into the navigable water of the United States.

Section 301(b) of the Act requires the achievement, by not later than July 1, 1977, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best practicable control technology currently available as defined by the Administrator pursuant to Section 304(b) of the Act. Section 301(b) also requires the achievement by not later than July 1, 1983, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best available technology economically achievable which will result in reasonable further progress toward the national goal of eliminating the discharge of all pollutants, as determined in accordance with regulations issued by the Administrator pursuant to Section 304(b) of the Act. Section 306 of the Act requires the achievement by new sources of a Federal standard of performance providing for the control of the discharge of pollutants which reflects the greatest degree of effluent reduction which the Administrator determines to be achievable through the application of the best available demonstrated control technology, processes, operating methods, or other alternatives, including, where practicable, a standard permitting no discharge of pollutants. Section 304(b) of the Act requires the Administrator to publish within one year of enactment of the Act, regulations providing guidelines for effluent limitations setting forth the degree of effluent reduction attainable through the application of the best practicable control technology currently available and the degree of effluent reduction attainable through the application of the best control measures and practices achievable including treatment techniques, process and procedure innovations, operation methods and other alternatives. The regulations proposed herein set forth effluent limitations guidelines pursuant to Section 304(b) of the Act for the inorganic chemicals manufacturing point source category.

Section 306 of the Act requires the Administrator, within one year after a category of sources is included in a list published pursuant to Section 306(b) (1) (A) of the Act, to propose regulations establishing Federal standards of performance for new sources within such categories. The Administrator published in the Federal Register of January 16, 1973 (38 F.R. 1624), a list of 27 point source categories. Publication of the list constituted announcement of the Administrator's intention of establishing, under Section 306, standards of performance applicable to new sources within the inorganic chemicals manufacturing point source category, which was included within the list published January 16, 1973.

SUMMARY OF METHODS USED FOR DEVELOPMENT OF EFFLUENT LIMITATION GUIDELINES AND STANDARDS OF PERFORMANCE

The Environmental Protection Agency has determined that a rigorous approach including plant surveying and verification testing is necessary for the development of effluent standards for industrial sources. A systematic approach to develop the required guidelines and standards includes the following:

(a) Categorization of the industry and determination of those industrial categories for which separate effluent limitations and standards need to be set;
(b) Characterization of the waste loads resulting from discharges within industrial categories and subcategories;
(c) Identification of the range of control and treatment technology within each industrial category and subcategory;
(d) Identification of those plants employing the best practical technology currently available (exemplary plants); and
(e) Generation of supporting verification data for the best practical technology including actual sampling of plant effluents by field teams.

The culmination of these activities is the development of the guidelines and standards based on the best practicable technology currently available.

This report describes the results obtained from application of the above approach to the inorganic chemicals industry. Thus, the survey and testing covered a wide range of processes, products, and types of wastes. Studies of a total of twenty-five chemicals listed below are summarized in this Document.

Selected Inorganic Chemicals

Aluminum Chloride
Aluminum Sulfate
Calcium Carbide
Calcium Chloride
Chlorine
Hydrochloric Acid
Hydrogen Peroxide

Potassium Sulfate
Sodium Bicarbonate
Sodium Carbonate (Soda Ash)
Sodium Chloride
Sodium Dichromate
Sodium Hydroxide
Sodium Metal

Hydrofluoric Acid
Calcium Oxide and Calcium Hydroxide
Nitric Acid
Potassium Chromates
Potassium Hydroxide
Potassium Metal
Sodium Silicate
Sodium Sulfate

Sodium Sulfite
Sulfuric Acid
Titanium Dioxide

The effluent limitation guidelines for existing point sources and standards of performance for new facilities were developed in the following manner. The point source category was first categorized for the purpose of determining whether separate limitations and standards are appropriate for different segments within a point source category. Such subcategorization was based upon raw material used, product produced, manufacturing process employed, and other factors. The raw waste characteristics for each subcategory were then identified. This included an analysis of (1) the source and volume of water used in the process employed and the sources of waste and waste waters in the plant; and (2) the constituents of all waste waters which result in degradation of the receiving water. The constituents of waste waters which should be subject to effluent limitations guidelines and standards of performance were identified.

The full range of control and treatment technologies existing within each subcategory was identified. This included an identification of each control and treatment technology, including both inplant and end-of-process technologies, which are existent or capable of being designed for each subcategory. It also included an identification of the quantity of constituents (including thermal) and the characteristics of pollutants resulting from the application of each of the treatment and control technologies. The problems, limitations and reliability of each treatment and control technology were also identified. In addition, the non-water quality environmental impact, such as the effects of the application of such technologies upon other pollution problems, including air, solid waste, noise and radiation were also identified. The energy requirements of each of the control and treatment technologies were identified as well as the cost of the application of such technologies.

Cost information contained in this report was obtained directly from industry during exemplary plant visits, from engineering firms and equipment suppliers, and from the literature. The information obtained from the latter three sources has been used to develop general capital, operating and overall costs for each treatment and control method. Costs have been put on a consistent industrial calculation basis of ten year straight line depreciation, plus allowance for interest at six percent per year (pollution abatement tax free money) and inclusion of allowance for insurance and taxes for an overall fixed cost amortization of fifteen percent per year. This generalized cost data, plus the specific information obtained from plant visits, was then used for cost effectiveness estimates in Section VIII and wherever else costs are mentioned in this Document.

The data for identification and analyses were derived from a number of sources. These sources included EPA research information, published literature, qualified technical consultation, on-site visits and interviews at numerous inorganic chemical plants throughout the U.S., interviews and meetings with various trade associations, and interviews and meetings with various regional offices of the EPA. All references used in developing the guidelines for effluent limitations and standards of performance for new sources reported herein are included in Section XIII.

Exemplary plant selection

Eleven corporate headquarters were initially consulted for assistance in preparing a list of potentially exemplary plants. Eighty plants were studied in depth by consultations and review of plant data. Of these, sixty plants were visited for additional screening and data collection. Twenty-eight plants were then visited and sampled by the contractor. This sampling included all of the chemical processes subject to effluent limitations guidelines. The following criteria were developed and used for the selection of exemplary plants.

(a) Discharge effluent quantities

Plants discharging small quantities of pollutants or no process waste water pollutants were preferred. This minimal discharge may be due to reuse of water, raw material recovery and recycling, or good water conservation. The significant parameter was minimal waste added to effluent streams per weight of product manufactured.

(b) Water management practices

Use of good management practices such as water reuse, planning and in-plant water segregation, and the proximity of cooling towers to operating units, where airborne contamination of water can occur, were considered.

(c) Land utilization

The efficiency of land use was considered.

(d) Air pollution and solid waste control

Exemplary plants must possess overall effective air and solid waste pollution control in addition to water pollution control technology. Care was taken to insure that all plants chosen have minimal discharges into the environment and that exemplary sites are not those which are exchanging one form of pollution for another of the same or greater magnitude.

(e) Effluent treatment methods and their effectiveness

Plants selected generally have in use the best currently available treatment methods, operating controls, and operational reliability. Treatment methods considered included basic process modifications which significantly reduce effluent loads as well as conventional end-of-pipe treatment methods.

(f) Plant facilities

All plants chosen as exemplary had all the facilities normally associated with the production of the specific chemical(s) in question. These facilities, generally, were plants which have all their normal process steps carried out on-site.

(g) Plant management philosophy

Plants were preferred whose management insists upon effective equipment maintenance and good housekeeping practices. These qualities are best identified by a high operational factor and plant cleanliness.

(h) Diversity of processes

On the basis that all of the above criteria are met, consideration was given to installations having a multiplicity of manufacturing processes. However, for sampling purposes, the complex facilities chosen were those for which the wastes could be clearly traced through the various treatment steps.

(i) Product purity

For cases in which purity requirements play a major role in determining the amounts of wastes to be treated and the degree of water recycling possible, different product grades were considered for sub-categorization.

Sampling of Exemplary Plants

The details of how the exemplary plants were sampled and the analytical techniques employed are fully discussed in Section V.

GENERAL DESCRIPTION OF THE INDUSTRY

Brief descriptions of each of the twenty-two chemical subcategories are presented below. Process flow sheets for the various subcategories are included. Production tonnages reported for 1971 were taken from Current Industrial Reports, Inorganic

Chemicals, U.S. Bureau of Census, Series M28A(71)-14.(1) These values are summarized in Table 2. Also included are production tonnages for years prior and subsequent to 1971, where available, and the number of plants producing each chemical.

Aluminum Chloride

The anhydrous product is produced by the reaction of gaseous chlorine with molten aluminum metal (scrap or scrap-pig mixture). The basic equation is:

$$2Al + 3Cl_2 \quad 2AlCl_3$$

Chlorine is introduced below the surface of the molten aluminum. The product sublimes and is collected by condensation. There are three types of products manufactured, all from the same general process:

(1) Yellow - this product is made using a slight excess of chloride (0.0005 percent) and may contain some iron due to reaction of the chloride with the vessel;
(2) White - this product has a stoichoimetric aluminum and chlorine starting ratio; and
(3) Grey - this product contains 0.01 percent excess aluminum. The unreacted aluminum raw waste load is higher for this grey material.

In most cases it makes little difference which of the above grades is employed. In some pigment and dye intermediate applications, the yellow material is preferred because it is free of elemental aluminum.

Aluminum chloride is also made from the reaction of bauxite, coke and chlorine. About 80 percent of all aluminum chloride made is anhydrous. A solution grade of aluminum chloride is also produced by reacting hydrated aluminum or bauxite ore with hydrochloric acid. A standard process diagram is shown in Figure 1.

Annual U.S. production in 1971 totalled 26,399 kkg (29,100 tons). The major use is as a catalyst in the petrochemical and synthetic polymer industries.

The 1971 production for the 28 percent solution product was 7,650 kkg (8,400 tons).

Aluminum Sulfate

Aluminum sulfate is produced by the reaction of bauxite ore, or other aluminum-containing compounds, with concentrated sulfuric acid (60°Be). The general equation of the reaction is:

$$Al_2O_3 \cdot 2H_2O + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 5H_2O$$

TABLE 2. U.S. Production of Inorganic Chemicals (Metric Tons)

	1973 (Est.)	1972	1971	1970	1969	No. of Plants (1971)
$AlCl_3$		30,844	26,399	28,485	35,834	5
$Al_2(SO_4)_3$		1,019,670	1,084,080	1,080,451	1,136,696	100
CaC_2		447,240	566,988	717,579	776,546	7
$CaCl_2$		861,821	1,100,409	1,006,000	1,066,843	9
Cl_2(g)	9,480,031	8,952,052	8,483,947	8,857,700	7,801,748	63
HCl	2,131,873	1,996,703	1,904,171	1,827,060	1,733,621	83
HF		301,184	199,126	203,571	200,940	13
H_2O_2		68,039	58,060	55,338	58,967	5
Lime					15,422,060	97
HNO_3	6,731,276	6,369,311	6,116,208	6,059,055	5,844,960	72
$K_2Cr_2O_7$		(Estimated)4,309				2
KOH		161,478	179,622	158,756	160,570	13
K	91		59	285		1
K_2SO_4			407,959	296,285	277,143	7
$NaHCO_3$			158,756	129,727	124,284	5
Na_2CO_3, total		6,768,470	6,396,526		6,350,260	13
Synthetic	3,991,592	3,929,904	3,878,194	3,985,242	4,118,597	7
NaCl					39,008,740	85
NaCl (Solar)			2,350,000			6
NaCl (Solution Mining)			5,928,000			?
$Na_2Cr_2O_7$ (& Chromate)		124,284	125,191	139,706	138,798	6
NaOH	9,797,544	9,196,084	9,276,006	9,199,712	8,996,504	62
Na			138,799	155,128	149,685	5
Sodium Silicate		601,460	569,709	569,709	596,017	33
Na_2SO_4		1,236,486	1,230,136	1,245,558	1,341,719	40
Na_2SO_3			185,065	222,259	205,930	6
H_2SO_4	29,664,786	27,257,130	26,691,000	26,784,489	26,795,375	150
TiO_2	644,098	623,233	615,068	594,203	602,367	14

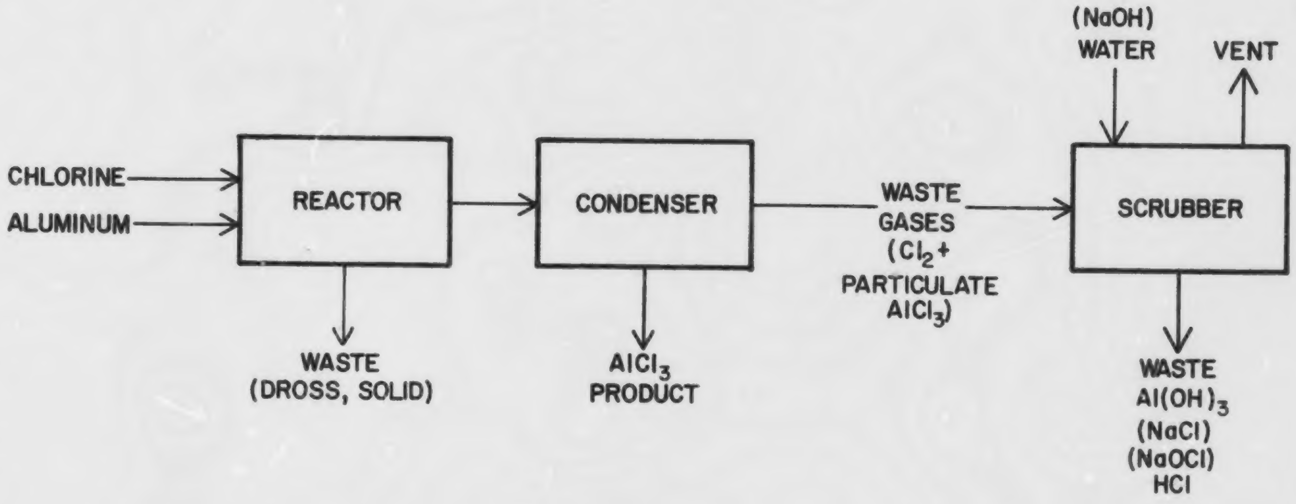

CHLORINE
ALUMINUM
REACTOR
WASTE (DROSS, SOLID)
CONDENSER
$AlCl_3$ PRODUCT
WASTE GASES (Cl_2 + PARTICULATE $AlCl_3$)
(NaOH) WATER
VENT
SCRUBBER
WASTE
$Al(OH)_3$
(NaCl)
(NaOCl)
HCl

FIGURE 1
STANDARD
ALUMINUM CHLORIDE FLOW DIAGRAM

Ground ore and acid are reacted in a digester, from which the products, aluminum sulfate in solution plus muds and other insoluble materials from the ore, are fed into a settling tank. The aluminum sulfate solution is then clarified and filtered to remove any remaining insolubles. It may be sold as solution or evaporated to yield a solid product. A typical process diagram is shown in Figure 2.

Annual U.S. production in 1971 was 1,084,080 kkg (1,195,000 tons). Aluminum sulfate, or filter alum, is used for water treatment (flocculation and clarification) and in treatment of paper mill waste, sewage, and other waste streams.

Calcium Carbide

This chemical is prepared by the reaction of calcium oxide with carbon (in the form of coke, petroleum coke, or anthracite) at 2000-2200°C (3632-3992°F) in a furnace similar to the familiar arc furnace, as shown in Figure 3. The general equation for the reaction is:

$$2CaO + 4C + Heat \longrightarrow 2CaC_2 + O_2$$

Calcium carbide is used primarily in the manufacturing of acetylene (by reaction with water). This use and the tonnage production has been steadily decreasing. Still, many calcium carbide plants are located in conjunction with acetylene plants. Since the production process is dry, the only major discharges are those effluents from scrubbing furnace and kiln offgases. The U.S. production in 1971 was 567,182 kkg (625,338 tons).

Calcium Chloride

Most of the calcium chloride produced is extracted from impure natural brines, but some of this salt is recovered as a by-product of soda ash manufacture by the Solvay process. In the manufacturing of calcium chloride from brine, the salts are solution mined and the resulting brines are first concentrated to remove sodium chloride by precipitation and then purified by the addition of other materials to precipitate sodium, potassium, and magnesium salts. The purified calcium chloride brine is then evaporated to yield a wet solid which is flaked and calcined to a dry solid product. Extensive recycling of partially purified brine is used to recover most of the sodium chloride values. A standard process diagram is shown in Figure 4.

Manufacture of calcium chloride from Solvay process waste liquors is similar to the natural brine process, except that the stepwise concentration and purification is unnecessary because no magnesium is present. Evaporation and calcining procedures are similar to those above. Significant wastes result from calcium chloride manufacturing.

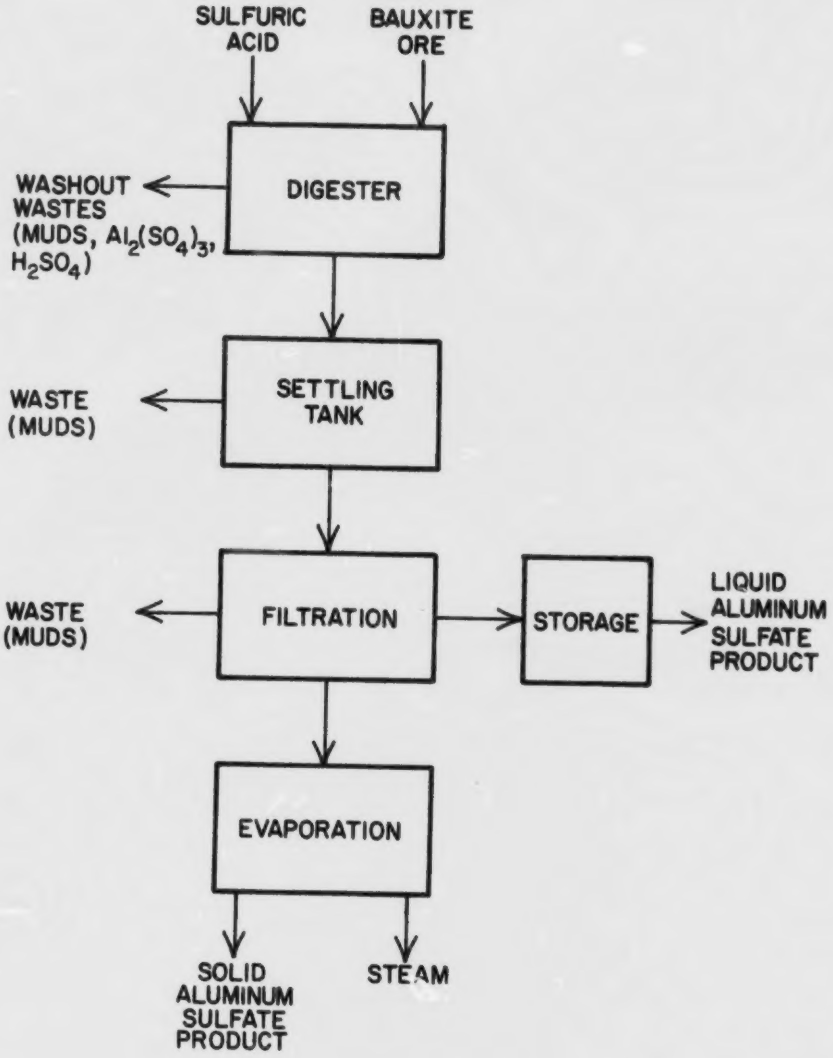

SULFURIC ACID
BAUXITE ORE
DIGESTER
WASHOUT WASTES (MUDS, $Al_2(SO_4)_3$, H_2SO_4)
SETTLING TANK
WASTE (MUDS)
FILTRATION
WASTE (MUDS)
STORAGE
LIQUID ALUMINUM SULFATE PRODUCT
EVAPORATION
SOLID ALUMINUM SULFATE PRODUCT
STEAM

FIGURE 2
STANDARD PROCESS DIAGRAM FOR ALUMINUM SULFATE MANUFACTURE

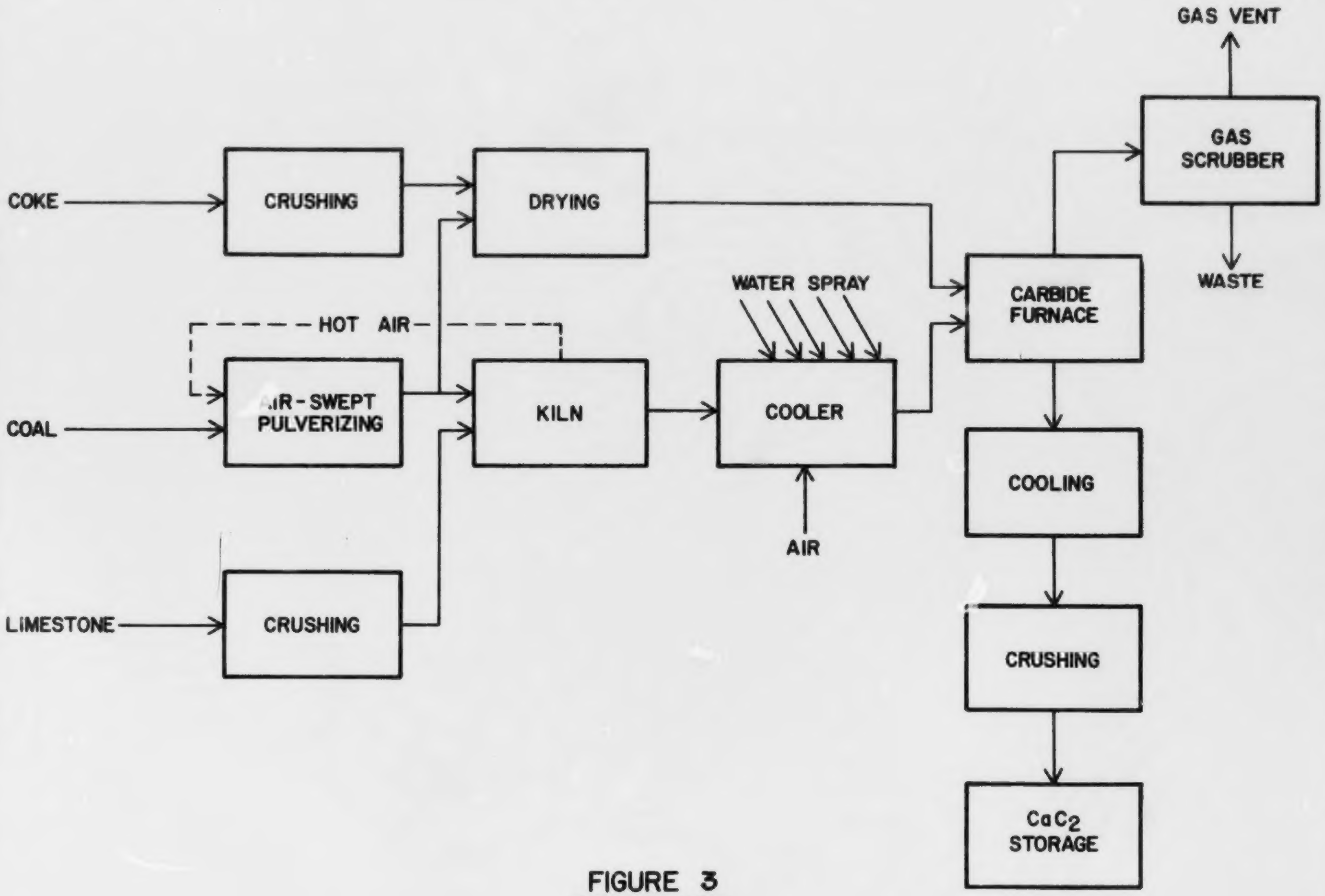

COKE
CRUSHING
DRYING
COAL
HOT AIR
AIR-SWEPT PULVERIZING
KILN
LIMESTONE
CRUSHING
WATER SPRAY
COOLER
AIR
CARBIDE FURNACE
GAS SCRUBBER
GAS VENT
WASTE
COOLING
CRUSHING
CaC_2 STORAGE

FIGURE 3
STANDARD
CALCIUM CARBIDE FLOW DIAGRAM

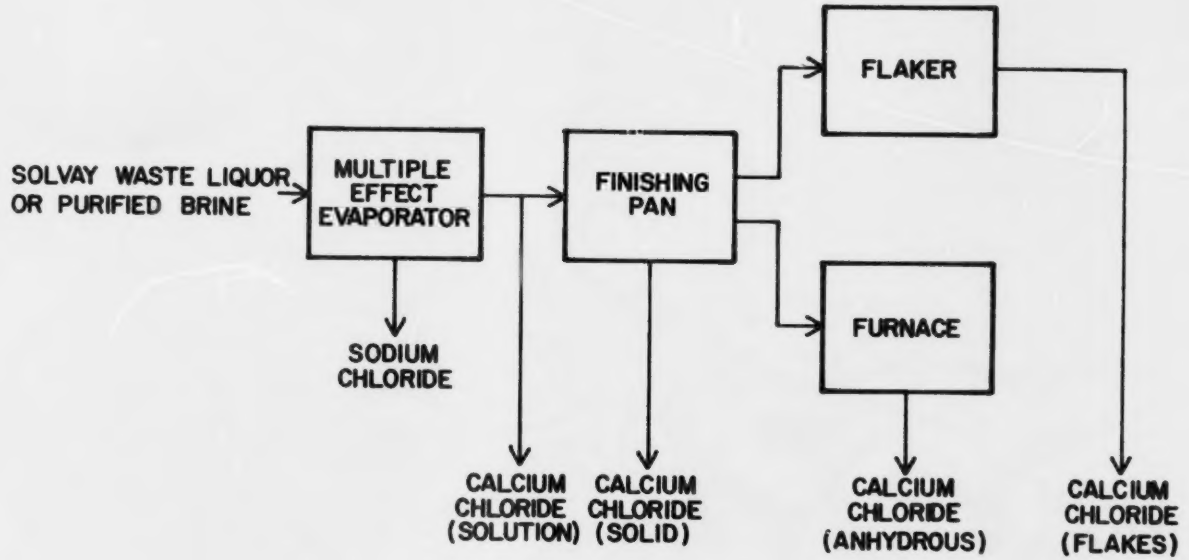

SOLVAY WASTE LIQUOR OR PURIFIED BRINE
MULTIPLE EFFECT EVAPORATOR
SODIUM CHLORIDE
FINISHING PAN
CALCIUM CHLORIDE (SOLUTION)
CALCIUM CHLORIDE (SOLID)
FLAKER
FURNACE
CALCIUM CHLORIDE (ANHYDROUS)
CALCIUM CHLORIDE (FLAKES)

FIGURE 4
STANDARD PROCESS FOR CALCIUM CHLORIDE MANUFACTURE

In 1971, U.S. production of calcium chloride was 1,101,281 kkg (1,213,000 tons). Uses include de-icing of roads, use as a stabilizer in pavement and cement, and dust control on roads. Production is increasing as more uses and markets are found, but potential production capability is much greater than that presently utilized. Recently, increased recovery resulting from pollution abatement measures has tended to cause calcium chloride supply to exceed demand. Plants recovering this salt from natural brines are located near mixed salt deposits, such as those in Michigan, West Virginia, and California.

Calcium Oxide and Calcium Hydroxide

Calcium oxide is produced by calcining various types of limestone in a continuous vertical or rotary kiln. The general equation for the reaction is:

$$CaCO_3 + Heat \rightarrow CaO + CO_2$$

Formerly coal or coke was used as fuel in vertical kilns, but in recent years large gas-fired kilns have been widely used. After calcination, the calcium oxide is cooled and then packaged or crushed and screened to yield a pulverized product. It may be slaked by reaction with water to yield calcium hydroxide and then marketed. The only waterborne wastes result from wet scrubbing of the gaseous kiln effluent to remove particulates. These wastes are high pH liquors which also contain suspended solids. The standard process diagram is shown in Figure 5.

Annual U.S. production of lime is believed to total about 16,000,000 kkg (17,600,000 tons). Approximately 20 percent of this production is "captive" (made and consumed in the same facility), primarily in the sugar, alkali, and steel industries. The remainder finds a variety of chemical and industrial uses, including use as an alkali and use in hydrated lime manufacturing. Principal growth areas appear to be in basic oxygen steel production and in soil stabilization.

Chlorine, Sodium or Potassium Hydroxide

The major chlorine production results from the electrolysis of sodium or potassium chloride brines, in which caustic soda (NaOH) or caustic potash (KOH), respectively, are also produced. The general equation for the electrolysis is (where M can be either Na or K):

$$3\ MCl + 2H_2O \xrightarrow{dc} Cl_2 + 2MOH + H_2$$

From the above equation it can be seen that hydrogen is also a by-product of brine electrolysis.

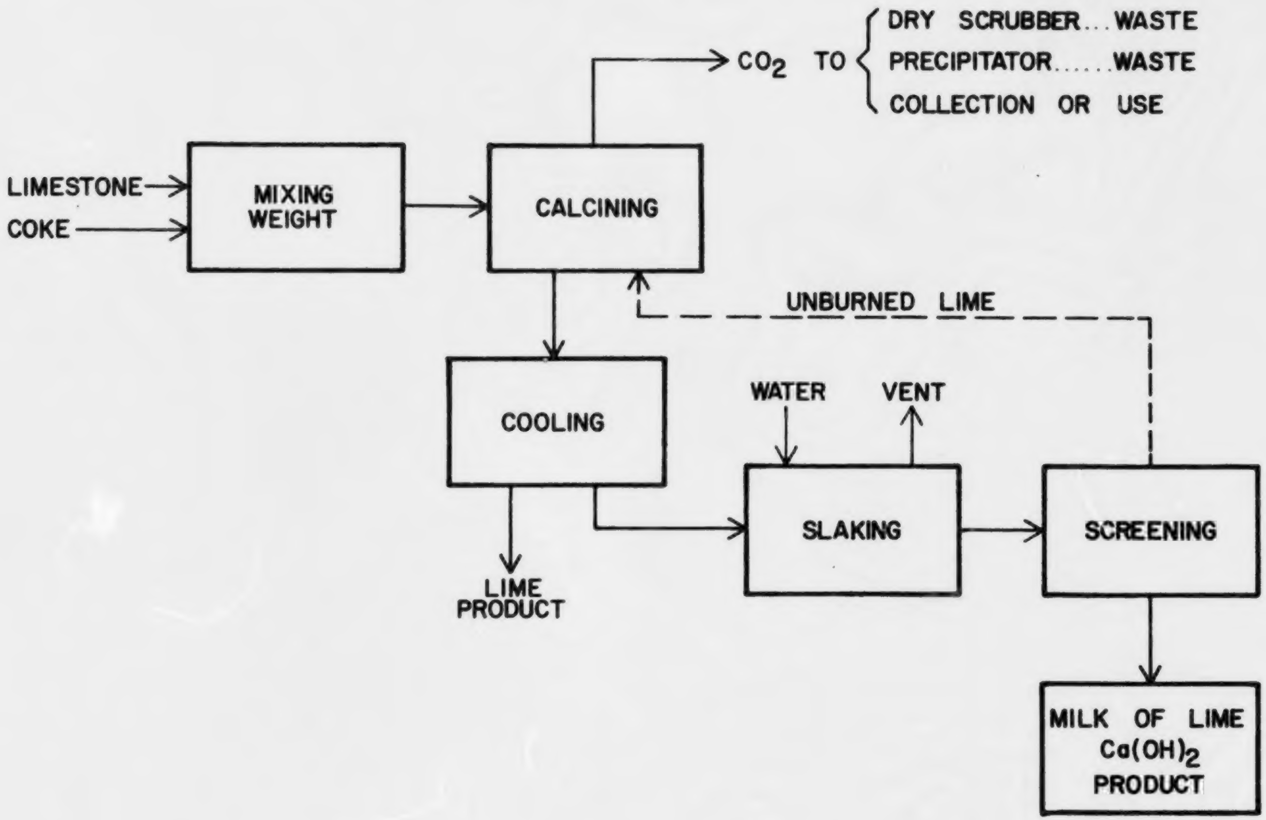

LIMESTONE
COKE
MIXING WEIGHT
CALCINING
CO_2 TO
DRY SCRUBBER... WASTE
PRECIPITATOR...... WASTE
COLLECTION OR USE
UNBURNED LIME
COOLING
LIME PRODUCT
WATER
VENT
SLAKING
SCREENING
MILK OF LIME
$Ca(OH)_2$
PRODUCT

FIGURE 5
STANDARD
CALCIUM OXIDE (LIME) FLOW DIAGRAM

Other sources (minor in size) of chlorine include the manufacture of hydrochloric acid and metallic sodium.

Two types of electrolysis cells are used, mercury cells and diaphragm cells.

a) Diaphragm cell process

In the diaphragm cell process, Figure 6, sodium chloride brines are first purified by addition of sodium carbonate, lime flocculating agents and barium carbonate in the amounts required to precipitate all the magnesium, calcium and sulfate contents of the brine. The brine is filtered to remove the precipitated materials and is then electrolyzed in a diaphragm cell. Chlorine, formed at one electrode, is collected, cooled, dried with sulfuric acid, then purified, compressed, liquified and shipped. At the other electrode, sodium hydroxide is formed and hydrogen is liberated. The hydrogen is cooled, purified, compressed and sold and the sodium hydroxide formed, along with unreacted brine, is then evaporated at 50 percent concentration. During partial evaporation, most of the unreacted sodium chloride precipitates from the solution, which is then filtered. The collected sodium chloride is recycled to the process and the sodium hydroxide solutions are sold or further evaporated to yield solid products.

In cases where potassium hydroxide is manufactured as a co-product with chlorine, purified potassium chloride is used instead of sodium chloride as the starting material. Otherwise, the process is identical.

b) Mercury cell process

Figure 7 shows a standard process diagram for sodium hydroxide and chlorine production by the mercury cell process. The raw material salt, is dissolved and purified by addition of barium chloride, soda ash, and lime to remove magnesium and calcium salts and sulfates prior to electrolysis. The insolubles formed on addition of the treatment chemicals are filtered from the brine and the brine is fed to the mercury cell, wherein chlorine is liberated at one electrode and a sodium-mercury amalgam is formed at the other.

Mercury cells utilize mercury flowing along the bottom of a steel trough as the cathode. A multiple anode is comprised of horizontal graphite plates. Upon electrolysis the alkali metal forms an amalgam with the mercury. The amalgam is decomposed externally to the cell by the addition of water, which results in the formation of hydrogen.

The chlorine gas from the cells is collected, cooled, dried by contact with sulfuric acid, and then purified and liquified for

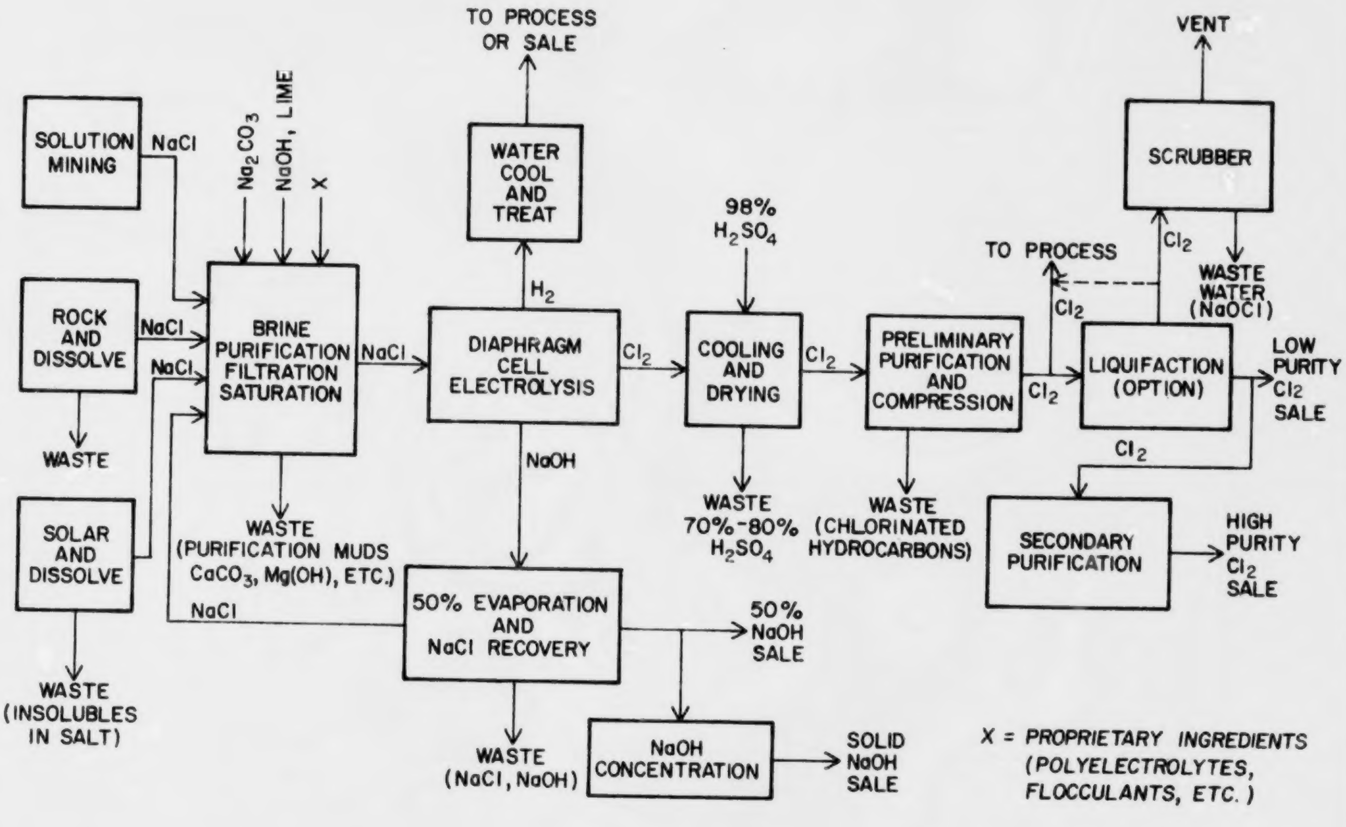
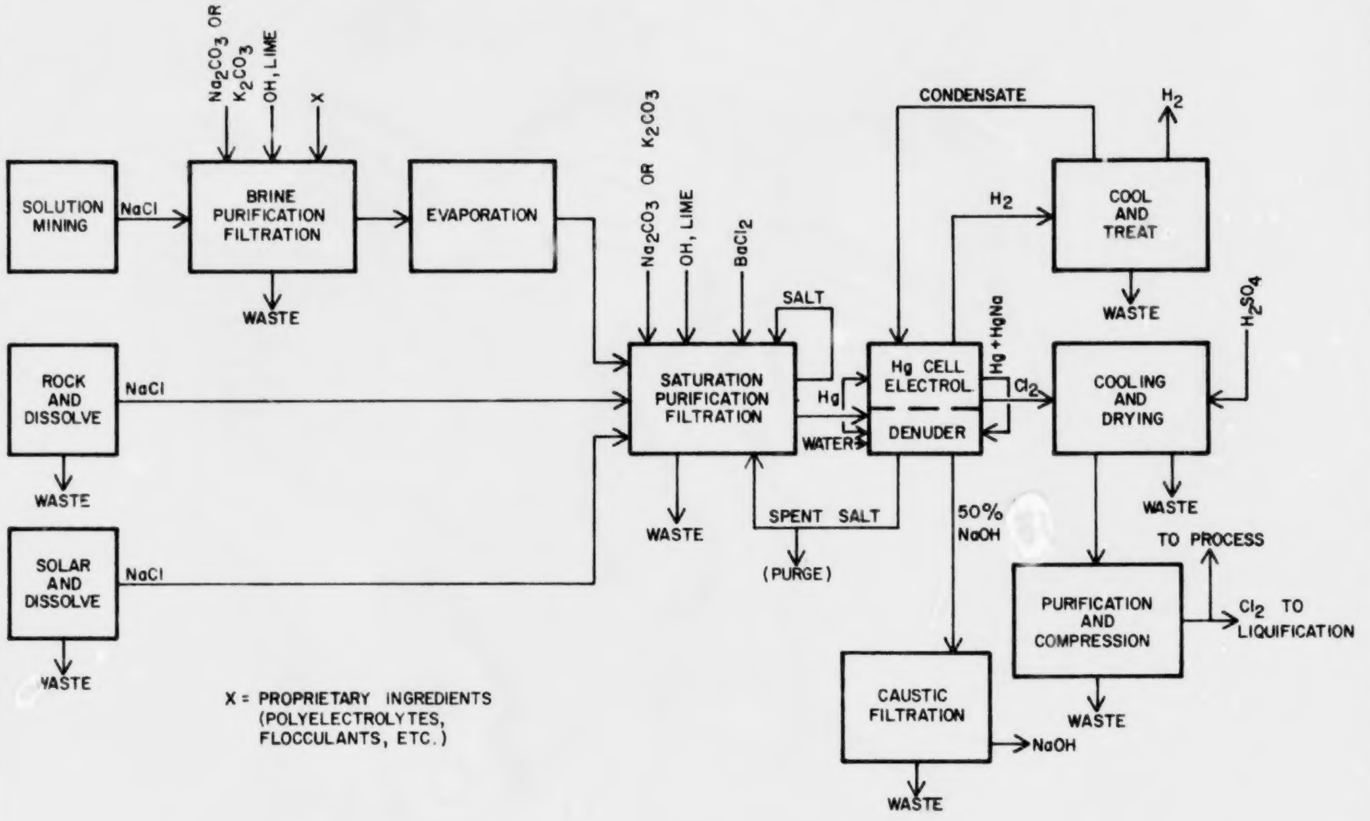

TO PROCESS OR SALE
VENT
SOLUTION MINING
NaCl
Na_2CO_3
NaOH, LIME
X
WATER COOL AND TREAT
98% H_2SO_4
SCRUBBER
TO PROCESS
Cl_2
WASTE WATER (NaOCl)
ROCK AND DISSOLVE
NaCl
NaCl
BRINE PURIFICATION FILTRATION SATURATION
NaCl
H_2
DIAPHRAGM CELL ELECTROLYSIS
Cl_2
COOLING AND DRYING
Cl_2
PRELIMINARY PURIFICATION AND COMPRESSION
Cl_2
Cl_2
LIQUIFACTION (OPTION)
LOW PURITY Cl_2 SALE
WASTE
NaOH
Cl_2
SOLAR AND DISSOLVE
WASTE (PURIFICATION MUDS $CaCO_3$, Mg(OH), ETC.)
WASTE 70%-80% H_2SO_4
WASTE (CHLORINATED HYDROCARBONS)
SECONDARY PURIFICATION
HIGH PURITY Cl_2 SALE
NaCl
50% EVAPORATION AND NaCl RECOVERY
50% NaOH SALE
WASTE (INSOLUBLES IN SALT)
WASTE (NaCl, NaOH)
NaOH CONCENTRATION
SOLID NaOH SALE
X = PROPRIETARY INGREDIENTS (POLYELECTROLYTES, FLOCCULANTS, ETC.)

FIGURE 6
STANDARD
CHLORINE-CAUSTIC SODA FLOW DIAGRAM - DIAPHRAGM CELL PROCESS


SOLUTION MINING
NaCl
Na_2CO_3 OR K_2CO_3
OH, LIME
X
BRINE PURIFICATION FILTRATION
WASTE
EVAPORATION
ROCK AND DISSOLVE
NaCl
WASTE
SOLAR AND DISSOLVE
NaCl
WASTE
Na_2CO_3 OR K_2CO_3
OH, LIME
$BaCl_2$
SALT
SATURATION PURIFICATION FILTRATION
WASTE
Hg
WATER
SPENT SALT
(PURGE)
CONDENSATE
H_2
Hg CELL ELECTROL.
DENUDER
Hg + HgNa
Cl_2
50% NaOH
CAUSTIC FILTRATION
NaOH
WASTE
COOL AND TREAT
H_2
WASTE
H_2SO_4
COOLING AND DRYING
WASTE
TO PROCESS
PURIFICATION AND COMPRESSION
Cl_2 TO LIQUIFICATION
WASTE

X = PROPRIETARY INGREDIENTS (POLYELECTROLYTES, FLOCCULANTS, ETC.)

FIGURE 7
STANDARD
CHLORINE-CAUSTIC FLOW DIAGRAM MERCURY CELL PROCESS

shipment, utilized on-site, or sold as gaseous chlorine. Much of the unreacted salt in the brine is recycled. Besides potential caustic and brine effluents some mercury is present in the spent brine from the mercury cell process. The cost of removing mercury from the effluent accounts, to some extent, for the shift back toward the diaphragm cells. Mercury cells began to be widely used in the early 1950's and reached a high of almost 30 percent of the total production in 1968.

The U.S. production of chlorine in 1971 totalled 8,482,660 kkg of gas (9,352,437 tons) and 4,035,489 kkg of liquid (4,449,271 tons). At present, about 75 percent of the production is in diaphragm cells, 20 percent in mercury cells, and 5 percent from other sources. About two-thirds of the production is utilized in the synthetic organic chemical and plastics industries, and half of that remaining is utilized in the pulp and paper industry (as a bleaching agent). Other uses include the inorganic chemicals industry, municipal water and sewage treatment, and many others. Somewhat over half of the total production is "captive", primarily in the synthetic organic chemicals and the pulp and paper industries. In recent years proximity to markets has been the major factor in chlorine plant location, in contrast to the cost of power and salt which previously dominated plant economics.

Sodium hydroxide is produced from the electrolysis of sodium chloride brines in mercury or diaphragm cells as described above. The caustic solution from the cathode of the electrolysis cell is evaporated to about 50 percent by weight sodium hydroxide. This may be sold as "standard-grade caustic liquor", concentrated to 73 percent, or further refined through removal of chloride and chlorate by various techniques. Refined caustic liquor may be sold, further concentrated to 73 percent solids, or evaporated to dryness. The anhydrous sodium hydroxide is sold in solid (flake or powdered) forms. Most of the product is sold in the liquid form.

Caustic soda has many varied uses, mostly as an alkali. It has also replaced soda ash (sodium carbonate) in many uses, such as in the aluminum industry and in other molten salt processes. It is used to manufacture soda ash in one plant. In 1971, the U.S. production of sodium hydroxide was 8,780,946 kkg (9,681,397 tons) in liquid form and 493,393 kkg (543,983 tons) in solid form.

Production methods for potassium hydroxide are very similar to those for sodium hydroxide, except that mined potassium chloride brines are used as the raw material. In the mercury cell process, the potassium-mercury amalgam is decomposed with water. The mercury is recycled and the caustic solution is cooled and filtered to recover potassium hydroxide.

The U.S. production of potassium hydroxide in 1971 was 179,760 kkg (198,192 tons). Caustic potash is used as an alkali, particularly when very high purity is desired or where other factors allow it to compete with sodium hydroxide (captive production, for instance). Other uses include the manufacturing of potassium salts and organic compounds containing potassium.

Hydrochloric Acid

There are two major processes used for hydrochloric acid manufacture. The process considered in this Document, as shown in Figure 8, is direct reaction of chlorine with hydrogen by:

$$Cl_2 + H_2 \rightarrow 2HCl$$

The second major source of production for hydrochloric acid, as a by-product of organic chlorination reactions, is the dominant source. This process is beyond the scope of this Document. By-product hydrochloric acid is typically of lower purity than that produced by direct reaction.

In the production of hydrochloric acid by direct reaction, hydrogen and chlorine gases are reacted in a vertical burner. The product hydrogen chloride so formed is cooled and then absorbed in water. Exhaust gases are scrubbed, and acid values are recycled. End products may include strong acid (22°Be) from the cooler, weak acid (18°Be) from the absorber column, a mixture of these (20°Be), or anhydrous HCl. The anhydrous acid may be prepared by stripping gaseous HCl from strong acid. The condensate and column bottoms from this process may then be recycled back into the hydrochloric acid recovery process.

Approximately 90 percent of the current production is byproduct, and supply often exceeds demand. Uses include pickling of steel, chlorination reactions (in place of chlorine), and a variety of uses as an acid agent. Total U.S. production in 1971 was 1,904,075 kkg (2,099,371 tons).

Hydrofluoric Acid

Hydrofluoric acid is obtained by reacting the mineral fluorspar (CaF_2) with concentrated sulfuric acid in a furnace, as shown in Figure 9. The general reaction for this process is:

$$CaF_2 + H_2SO_4 + Heat \rightarrow H_2F_2 + CaSO_4$$

The hydrofluoric acid leaves the furnace as a gas, which is then cooled and absorbed in water prior to purification. In the purification system, the crude acid is redistilled and either absorbed in water to yield aqueous hydrofluoric acid or compressed and bottled for sale as anhydrous hydrofluoric acid. Final drying of the anhydrous gas is accomplished with

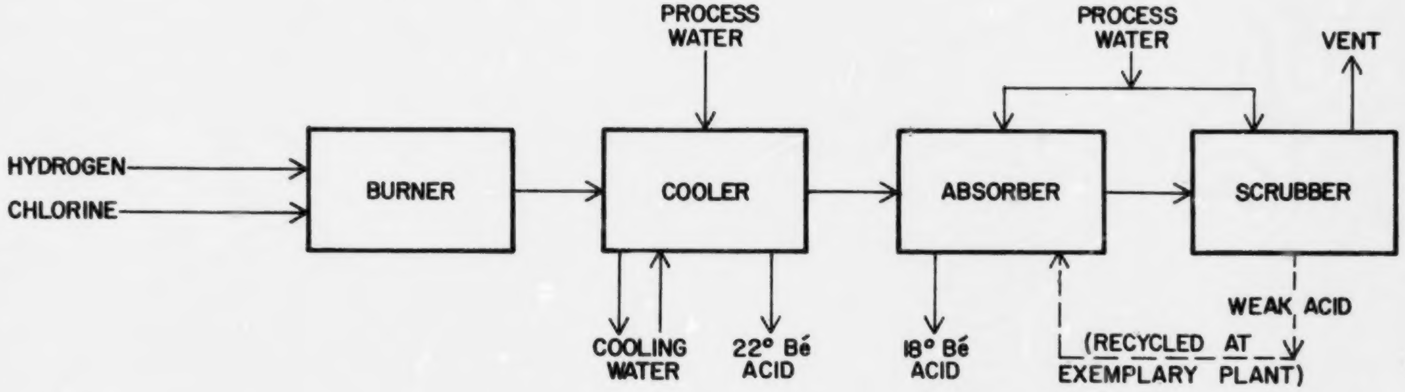

PROCESS WATER
PROCESS WATER
VENT
HYDROGEN
CHLORINE
BURNER
COOLER
ABSORBER
SCRUBBER
WEAK ACID
COOLING WATER
22° Bé ACID
18° Bé ACID
(RECYCLED AT EXEMPLARY PLANT)

FIGURE 8
STANDARD
HYDROCHLORIC ACID FLOW DIAGRAM (SYNTHETIC PROCESS)

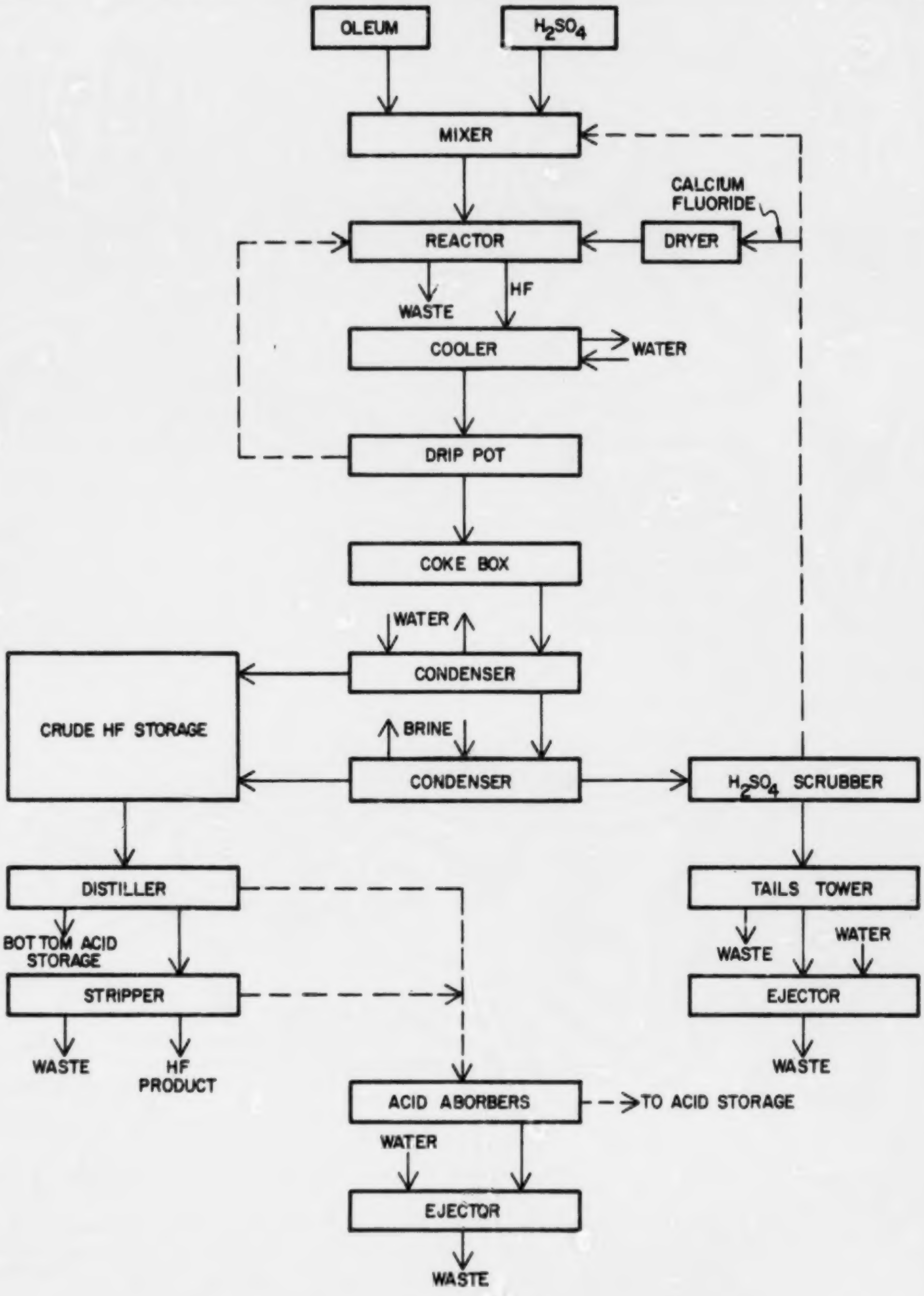

OLEUM
H_2SO_4
MIXER
CALCIUM FLUORIDE
REACTOR
DRYER
WASTE
HF
COOLER
WATER
DRIP POT
COKE BOX
WATER
CONDENSER
CRUDE HF STORAGE
BRINE
CONDENSER
H_2SO_4 SCRUBBER
DISTILLER
TAILS TOWER
BOTTOM ACID STORAGE
WASTE
WATER
STRIPPER
EJECTOR
WASTE
HF PRODUCT
WASTE
ACID ABORBERS
TO ACID STORAGE
WATER
EJECTOR
WASTE

FIGURE 9
HYDROFLUORIC ACID FLOW DIAGRAM

concentrated sulfuric acid. Aqueous acid is normally shipped as 70 percent acid.

Most U.S. hydrofluoric acid production (probably 75-80 percent) is captive to the fluorinated organics and plastics industries. Total U.S. production in 1971 was 199,069 kkg (219,481 tons), and the production appears to be increasing fairly rapidly. Fluorinated organics and plastics comprise the major use industries. Another major use is in the production of synthetic cryolite and aluminum fluoride. Most of the acid-grade fluorspar ore is imported. Waste disposal problems and safety hazards are specialized and severe because of the reactivity of the material.

Hydrogen Peroxide

Hydrogen peroxide is manufactured by three different processes: (1) An electrolytic process; (2) Oxidation of alkyl hydroanthraquinones; and (3) As a by-product in the manufacturing of acetone from isopropyl alcohol. This Document includes processes (1) and (2).

a) Electrolytic process

In the electrolytic process, a solution of ammonium (or other) bisulfate is electrolyzed, yielding ammonium persulfate at the anode and hydrogen gas at the cathode. The persulfate is then reacted with water (hydrolyzed) to yield hydrogen peroxide and the original bisulfate. The general reaction scheme is:

$$2NH_4HSO_4 \xrightarrow{dc} (NH_4)_2S_2O_8 + H_2$$
$$(NH_4)_2S_2O_8 + H_2O \rightarrow 2NH_4HSO_4 + H_2O_2$$

The crude peroxide product emerges mixed with water, and can be concentrated to desired levels by vacuum distillation or low-temperature fractionation. The cathode liquor is filtered and reused. A standard flow diagram is shown in Figure 10.

b) Organic process

The alkylhydroanthraquinone oxidation process is shown in general form below ("R" represents the alkylanthraquinone molecule, except for the two double-bonded oxygens):

$$O{=}R{=}O + H_2 \xrightarrow{Cat.} HO{-}R{-}OH$$
$$HO{-}R{-}OH + O_2 \rightarrow O{=}R{=}O + H_2O_2$$

In this process, the alkylanthraquinone is reduced by hydrogen over a supported metal catalyst (typically palladium on alumina), the product being the corresponding alkylhydroanthraquinone. This, in turn, is oxidized by oxygen in a forced gas stream to

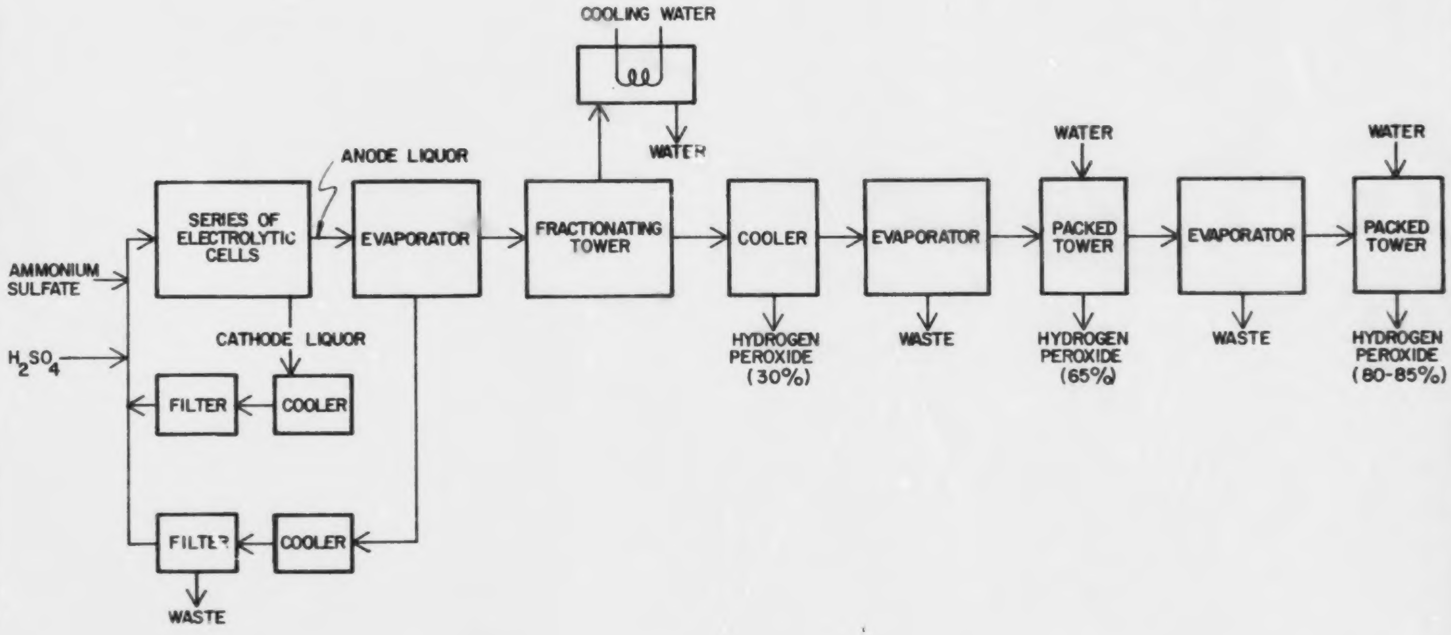

COOLING WATER
WATER
ANODE LIQUOR
AMMONIUM SULFATE
H_2SO_4
SERIES OF ELECTROLYTIC CELLS
CATHODE LIQUOR
EVAPORATOR
FILTER
COOLER
FILTER
COOLER
WASTE
FRACTIONATING TOWER
COOLER
HYDROGEN PEROXIDE (30%)
EVAPORATOR
WASTE
WATER
PACKED TOWER
HYDROGEN PEROXIDE (65%)
EVAPORATOR
WASTE
WATER
PACKED TOWER
HYDROGEN PEROXIDE (80-85%)

FIGURE 10

STANDARD HYDROGEN PEROXIDE ELETROLYTIC PROCESS FLOW DIAGRAM reform the original alkylanthraquinone plus hydrogen peroxide. The hydrogen peroxide is extracted with water and the alkylanthraquinone is recycled. The recovered product is then concentrated, purified, and sold. A general process diagram for the organic process is shown in Figure 11.

Hydrogen peroxide is sold in a range of aqueous concentrations from three percent to 98 percent by weight. The higher concentration materials are dangerously reactive. A stabilizer (such as acetanilid) is typically added to the product to retard decomposition. Uses include bleaching of textiles and paper, epoxidation, production of peroxy-acid catalysts, oxidation of organic compounds, formation of foams, and a source of energy for both military and civilian applications. The U.S. production in 1971 was 57,937 kkg (63,878 tons).

Nitric Acid

This document covers production of nitric acid in concentrations up to 68 percent by weight (azectropic concentration). More concentrated nitric acid, including fuming nitric acid and nitrogen pentoxide will be included in the Phase II Document. The production of nitric acid by the reaction of sodium nitrate and sulfuric acid is also not included.

Nitric acid is produced by the catalytic oxidation of ammonia, first to nitric oxide (NO), and then to nitrogen dioxide (NO_2), which is reacted with water under pressure to form the acid as shown in Figure 12. The overall reaction scheme is:

$$4NH_3 + 5O_2 \xrightarrow{\text{cat.}} 4NO + 6H_2O$$
$$2NO + O_2 \rightarrow 2NO_2$$
$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

In the process, compressed, purified, and preheated air and anhydrous ammonia are mixed and passed over a platinum rhodium wire-gauze catalyst at about 750°C (1382°F). The resultant mixture of nitric oxide and excess air is introduced, along with additional air, into a stainless steel absorption tower in which the nitric oxide is further oxidized. The resulting nitrogen dioxide is reacted with water. The bottm of the tower yields 61 - 65 percent by weight nitric acid.

Most of the U.S. nitric acid production is utilized in the fertilizer industry. The second largest use is in explosives manufacturing. Various uses as an acidic or pickling agent account for much of the remaining production. Total U.S. production in 1971 was 6,151,112 kkg (6,742,130 tons).

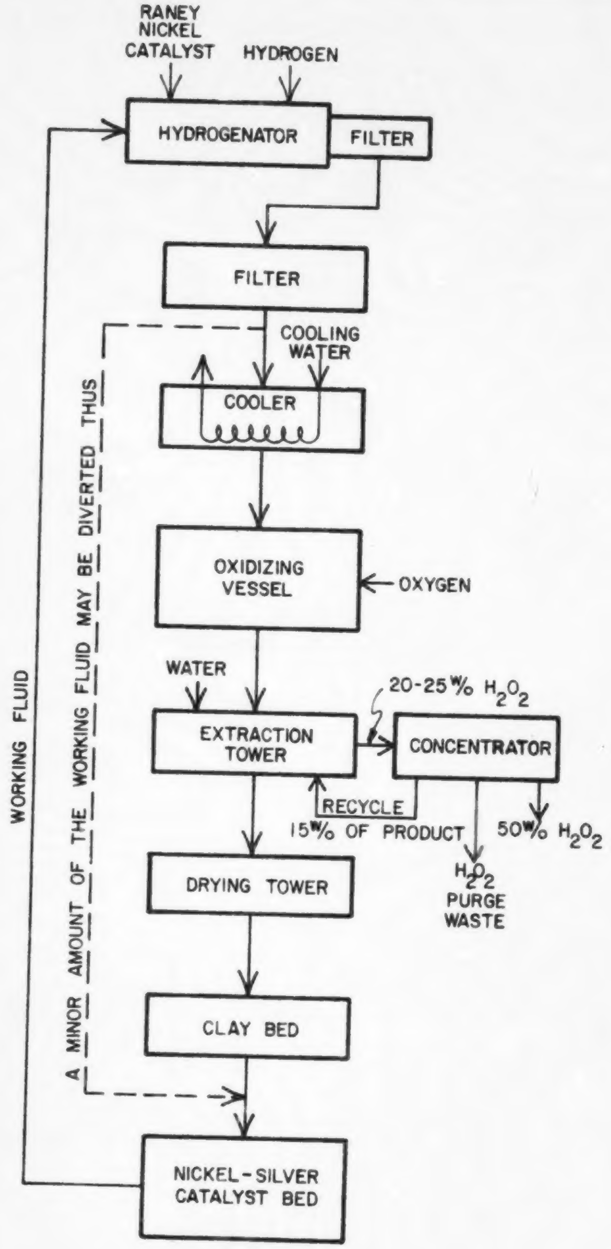

RANEY NICKEL CATALYST
HYDROGEN
HYDROGENATOR
FILTER
FILTER
COOLING WATER
COOLER
A MINOR AMOUNT OF THE WORKING FLUID MAY BE DIVERTED THUS
WORKING FLUID
OXIDIZING VESSEL
OXYGEN
WATER
20-25 w/o H_2O_2
EXTRACTION TOWER
CONCENTRATOR
RECYCLE
15 w/o OF PRODUCT
50 w/o H_2O_2
H_2O_2 PURGE WASTE
DRYING TOWER
CLAY BED
NICKEL-SILVER CATALYST BED

FIGURE 11
STANDARD
HYDROGEN PEROXIDE FLOW DIAGRAM
(RIEDL-PFLEIDERER PROCESS)

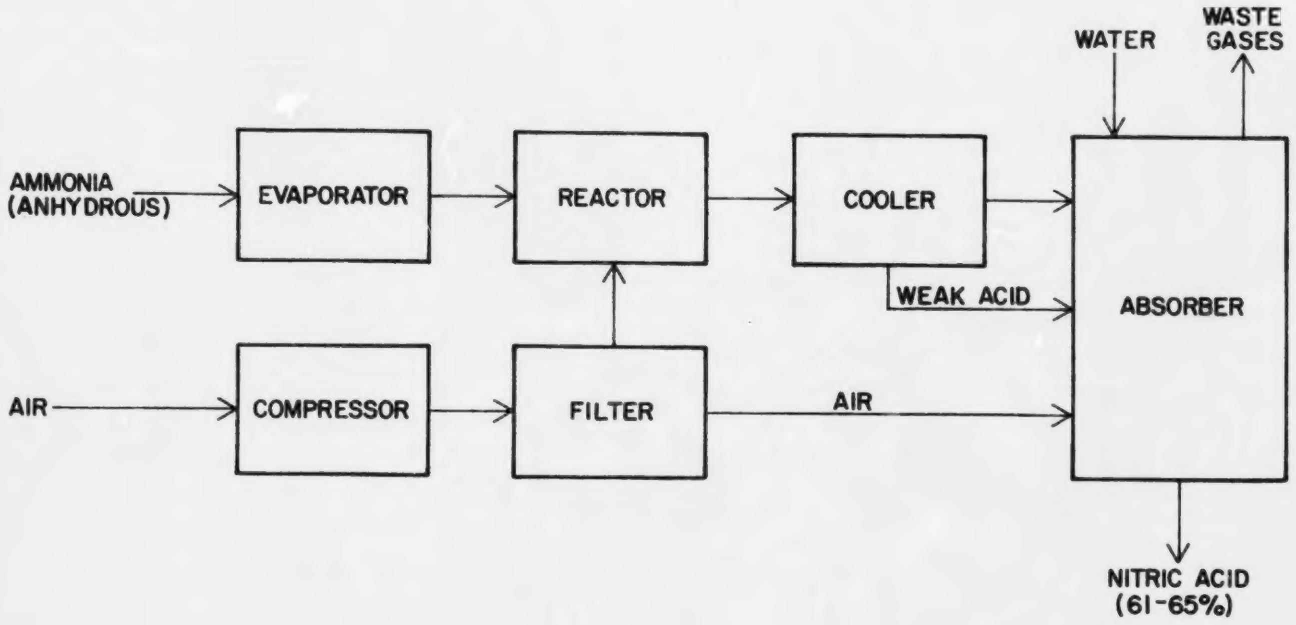

AMMONIA
(ANHYDROUS)
EVAPORATOR
REACTOR
COOLER
WATER
WASTE
GASES
WEAK ACID
ABSORBER
AIR
COMPRESSOR
FILTER
AIR
NITRIC ACID
(61-65%)

FIGURE 12
STANDARD NITRIC ACID PROCESS FLOW DIAGRAM

Potassium Metal

Potassium is produced by the reaction of potassium chloride with sodium vapor:

$$KCl + Na + Heat \rightarrow K + NaCl$$

For the commercial preparation of potassium metal, potassium chloride is melted in a gas fired melt pot and fed to an exchange column as shown in Figure 13. The molten potassium chloride flows over Raschig rings in the packed column, where it contacts ascending sodium vapors coming from a gas-fired reboiler. An equilibrium is established between the two, yielding sodium chloride and elemental potassium. The sodium chloride formed is continuously withdrawn at the base of the apparatus and is normally sold. The column operating conditions may be varied to yield either pure potassium metal as an overhead product or to vaporize sodium along with the potassium to produce sodium-potassium (NaK) alloys of varying compositions. Potassium metal of over 99.5 percent purity can be continuously produced.

Since it is relatively more reactive than sodium, the reaction between potassium and carbon (plus a tendency to form explosive carbonyls) precludes the manufacture of potassium by electrolysis. Because it is more expensive than sodium, potassium has very limited uses. Major uses include manufacture of organo-potassium compounds and production of NaK (sodium potassium alloys used in lard modification and as a nuclear reactor coolant). Total U.S. production in 1972 was about 100 kkg (110 tons), primarily from one facility.

Potassium Dichromate

Most of the potassium dichromate manufactured in the U.S. is made by reacting a sodium dichromate dihydrate solution with potassium chloride according to the following:

$$Na_2Cr_2O_7 \cdot 2H_2O + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl + 2H_2O$$

Potassium chloride is added to a dichromate solution, which is then pH adjusted, saturated, filtered and vacuum cooled to precipitate crystalline potassium dichromate which is recovered by centrifuging, dried, sized and packaged. The mother liquor from the product centrifuge is then concentrated to precipitate sodium chloride which is removed as a solid waste from a salt centrifuge. The process liquid is recycled to the initial reaction tank. Figure 14 is the standard process diagram. A relatively pure product results which requires only removal of the water prior to sizing and packaging.

The major uses of potassium dichromate are as a glass pigment and a photographic development chemical. Estimated annual production in the U.S. is 4,000-4,500 kkg (4,400-5,000 tons).

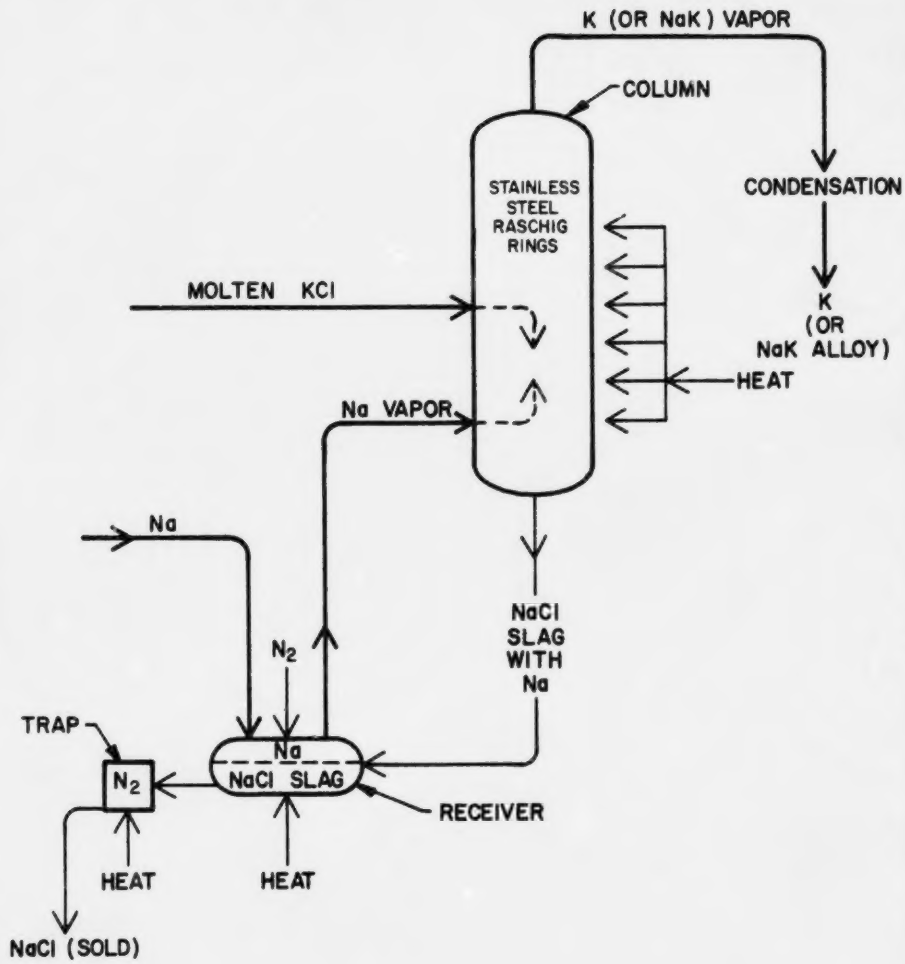

K (OR NaK) VAPOR
COLUMN
STAINLESS STEEL RASCHIG RINGS
CONDENSATION
K (OR NaK ALLOY)
MOLTEN KCl
HEAT
Na VAPOR
Na
N_2
NaCl SLAG WITH Na
TRAP
N_2
Na
NaCl SLAG
RECEIVER
HEAT
HEAT
NaCl (SOLD)

FIGURE 13
COMMERCIAL EXTRACTION OF POTASSIUM

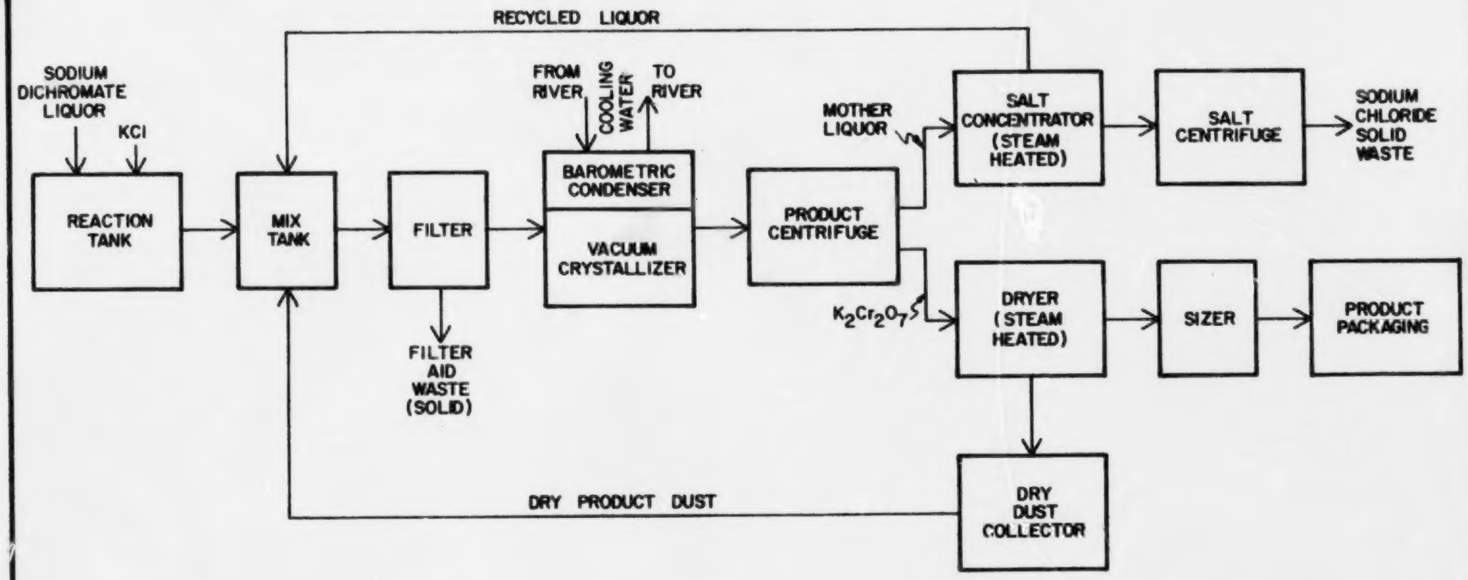

RECYCLED LIQUOR
SODIUM DICHROMATE LIQUOR
KCl
REACTION TANK
MIX TANK
FILTER
FILTER AID WASTE (SOLID)
FROM RIVER
COOLING WATER
TO RIVER
BAROMETRIC CONDENSER
VACUUM CRYSTALLIZER
PRODUCT CENTRIFUGE
MOTHER LIQUOR
$K_2Cr_2O_7$
SALT CONCENTRATOR (STEAM HEATED)
SALT CENTRIFUGE
SODIUM CHLORIDE SOLID WASTE
DRYER (STEAM HEATED)
SIZER
PRODUCT PACKAGING
DRY DUST COLLECTOR
DRY PRODUCT DUST

FIGURE 14
STANDARD POTASSIUM DICHROMATE PROCESS FLOW DIAGRAM

Potassium Sulfate

The bulk of the potassium sulfate manufactured in the U.S. is prepared by the treatment with potassium chloride of dissolved langbeinite, a naturally-occuring potassium sulfate-magnesium sulfate mineral, $K_2SO_4 \cdot 2MgSO_4$. Mined langbeinite is crushed and dissolved in water to which potassium chloride is added. Partial evaporation of the solution results in selective precipitation of potassium sulfate which is recovered by centrifugation or filtration, dried, and sold. The remaining brine liquor is either discharged to an evaporation pond, reused as process water, or evaporated. Magnesium chloride may be economically recovered as a byproduct if the raw material is of sufficiently high quality. A standard process diagram is shown in Figure 15. Current annual production in the U.S. is 407,916 kkg (449,742 tons). Much of this finds agricultural use, particularly for tobacco and citrus.

Sodium Bicarbonate

Sodium bicarbonate, also known as baking soda, is made by the reaction of sodium carbonate with water and carbon dioxide under pressure, as shown in Figure 16. The bicarbonate so formed precipitates from the solution and is filtered, washed, dried, and packaged. The general process reaction is:

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$$

Sodium bicarbonate is typically a minor by-product of soda ash manufacturers.

Total U.S. production in 1971 was 158,305 kkg (174,537 tons). Major industrial users include food processors, chemical plants, pharmaceutical producers, synthetic rubber manufacturers, leather processors and paper and textile producers. It is also used in fire extinguishers to form carbon dioxide and in food preparation.

Sodium Carbonate

Sodium carbonate, or soda ash, is produced by the "Solvay" process and by mining naturally-occuring deposits in California and Wyoming. Production by mining is less than that from the Solvay process. In the mining process, trona (sodium sesquicarbonate, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$) is brought to the surface in solid form, crushed and ground, and dissolved in water. The solution is clarified, thickened, filtered, and sent to vacuum crystallizers, from which part of the soda ash is recovered in solid form. The remaining solution is cooled to precipitate additional soda ash and bicarbonate. These solids are then dewatered and calcined to yield soda ash.

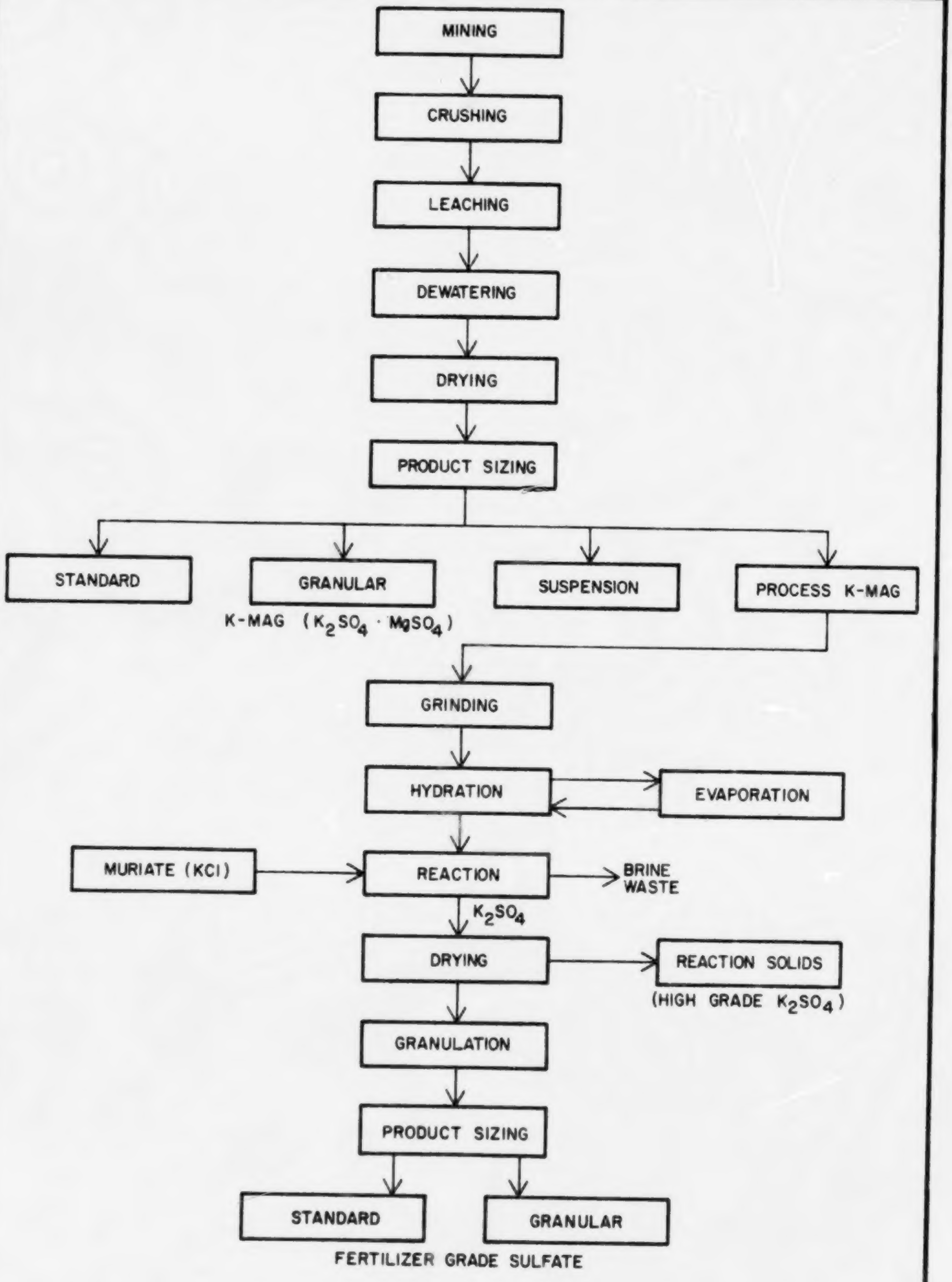

MINING
CRUSHING
LEACHING
DEWATERING
DRYING
PRODUCT SIZING
STANDARD
GRANULAR
SUSPENSION
PROCESS K-MAG
K-MAG ($K_2SO_4 \cdot MgSO_4$)
GRINDING
HYDRATION
EVAPORATION
MURIATE (KCl)
REACTION
BRINE WASTE
K_2SO_4
DRYING
REACTION SOLIDS
(HIGH GRADE K_2SO_4)
GRANULATION
PRODUCT SIZING
STANDARD
GRANULAR
FERTILIZER GRADE SULFATE

FIGURE 15
STANDARD POTASSIUM SULFATE PROCESS DIAGRAM

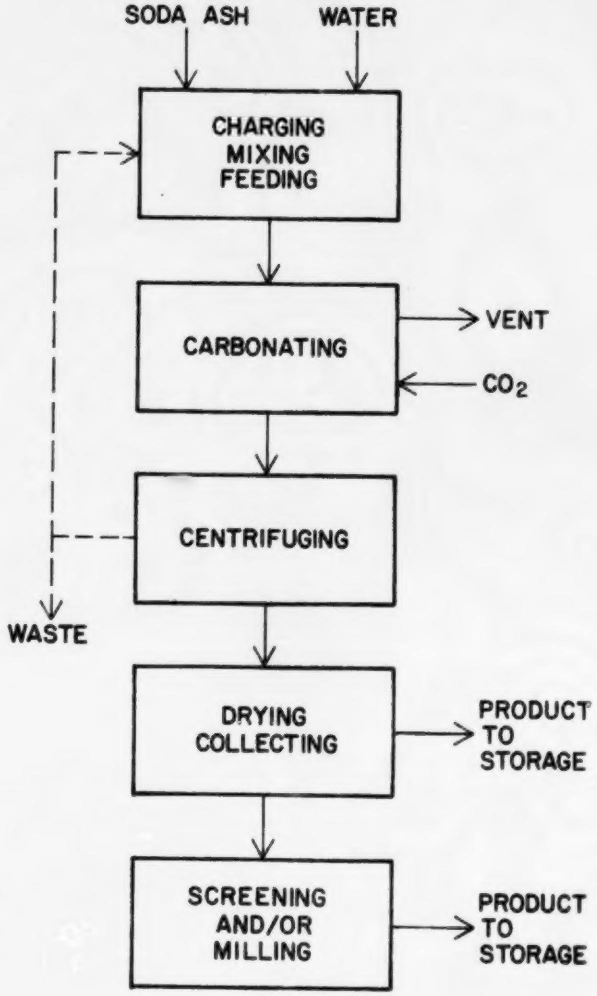

SODA ASH
WATER
CHARGING MIXING FEEDING
CARBONATING
VENT
CO_2
CENTRIFUGING
WASTE
DRYING COLLECTING
PRODUCT TO STORAGE
SCREENING AND/OR MILLING
PRODUCT TO STORAGE

FIGURE 16
STANDARD SODIUM BICARBONATE PROCESS FLOW DIAGRAM

The Solvay process, as shown in Figure 17, involves a reaction in aqueous solution (under pressure) between ammonia, brine (NaCl), and carbon dioxide to yield sodium bicarbonate, which is then converted to soda ash by heating. Ammonia is recovered by the addition of slaked lime to the used liquor. The general reaction is as follows:

Formation of Ammonium Bicarbonate
$NH_3 + H_2O \rightarrow NH_4OH$
$NH_4OH + CO_2 \rightarrow NH_4HCO_3$

Conversion to Sodium Bicarbonate
$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$

Conversion to Soda Ash
$2NaHCO_3 + Heat \rightarrow Na_2CO_3 + CO_2 + H_2O$

Recovery of Ammonia
$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + H_2O$

The saturated brine is purified of other metal ions by precipitation, and then picks up ammonia in an absorber tower. Ammoniated brine is reacted with carbon dioxide in a carbonating tower, and the resulting bicarbonate precipitates as the sodium salt, forming a slurry. The slurry is filtered to remove the solid bicarbonate which is calcined to yield the light ash product. Dense ash is made by successive hydration and dehydration of the light ash. The carbon dioxide and ammonia are recycled. Calcium chloride is also being recovered now in some plants.

Many soda ash plants are associated with producers of glass (largest user industry) or with sources or raw material such as coke-oven plants (by-product ammonia), the cement industry (utilization of lime sludge), or solid carbon dioxide producers. Soda ash competes with caustic soda and other chemicals in a variety of applications other than glass manufacture. Large amounts are used in the non-ferrous metals industry and in the production of bicarbonate and washing soda. Several types of products are sold commercially. Production figures for the U.S. in 1971 are as follows:

Finished Light Ash - 1,676,621 kkg (1,848,535 tons)
Finished Dense Ash - 2,120,467 kkg (2,337,891 tons)
Natural Ash - 2,598,321 kkg (2,864,742 tons)
Total - 6,395,409 kkg (7,051,168 tons)

Sodium Chloride

Large quantities of this chemical are produced from brine or seawater by three basic processes:

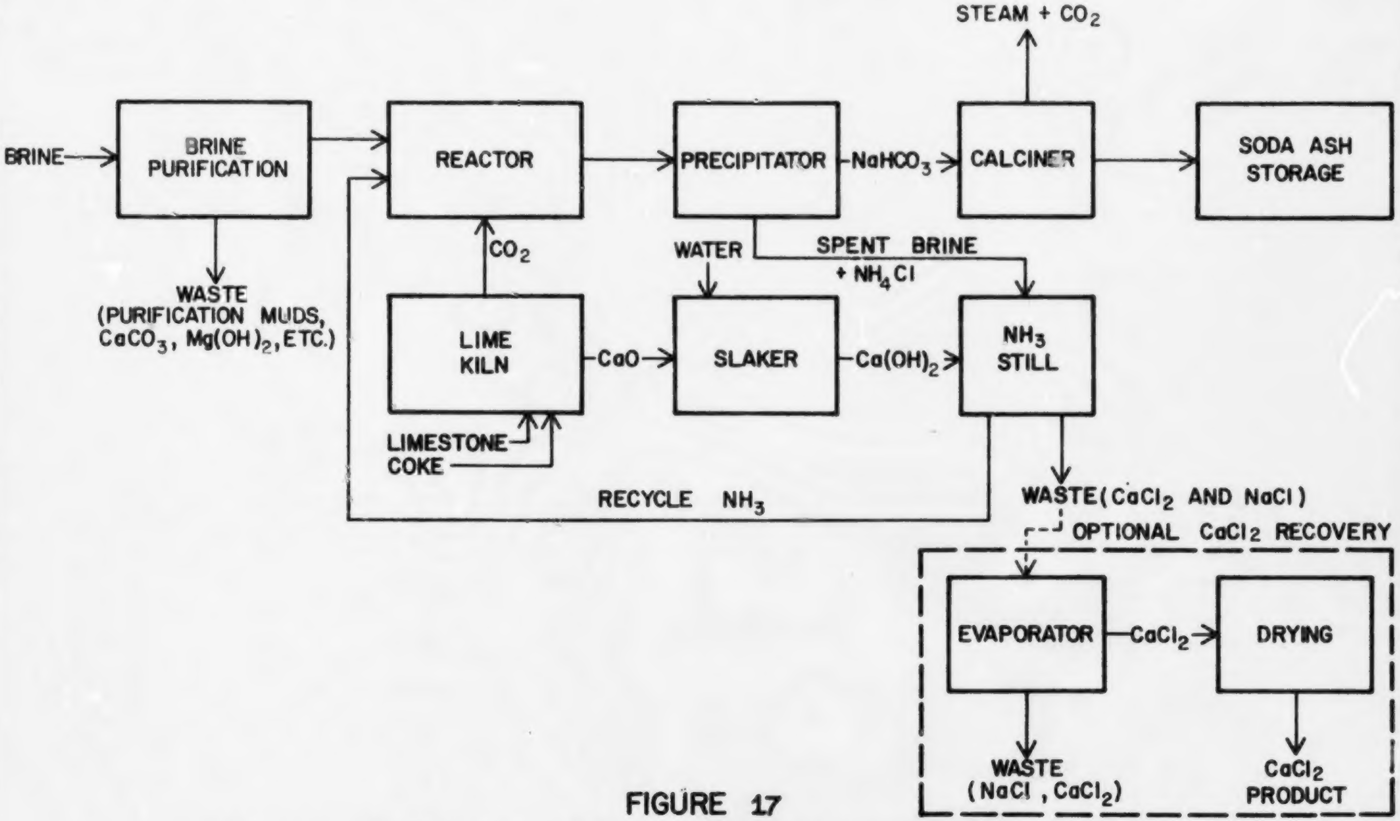

BRINE
BRINE PURIFICATION
WASTE (PURIFICATION MUDS, $CaCO_3$, $Mg(OH)_2$, ETC.)
REACTOR
CO_2
LIME KILN
LIMESTONE
COKE
CaO
WATER
SLAKER
$Ca(OH)_2$
PRECIPITATOR
$NaHCO_3$
SPENT BRINE + NH_4Cl
CALCINER
STEAM + CO_2
SODA ASH STORAGE
NH_3 STILL
RECYCLE NH_3
WASTE ($CaCl_2$ AND NaCl)
OPTIONAL $CaCl_2$ RECOVERY
EVAPORATOR
$CaCl_2$
DRYING
WASTE (NaCl, $CaCl_2$)
$CaCl_2$ PRODUCT

FIGURE 17

SOLVAY PROCESS SODIUM CARBONATE FLOW DIAGRAM

(1) solar evaporation of brine;
(2) solution mining of natural salt; and
(3) conventional mining of rock salt.

a) Solar evaporation process

In the solar evaporation process, salt water is concentrated by evaporation over a period of several years in open ponds to yield a saturated brine solution. After saturation is reached, the brine is then fed to a crystallizer, wherein sodium chloride precipitates, leaving behind a concentrated brine solution (bittern) consisting of sodium, potassium and magnesium salts. The precipitated sodium chloride is recovered for sale and the brine may be further evaporated to recover additional sodium chloride values and is either stored, discharged back to salt water or further worked to recover potassium and magnesium salts. A process diagram is shown in Figure 18.

b) Solution brine-mining process

Saturated brine for the production of evaporated salt is usually obtained by pumping water into an underground salt deposit and removing a saturated salt solution from an adjacent interconnected well, or from the same well by means of an annular pipe. Besides sodium chloride, the brine will normally contain some calcium sulfate, calcium chloride and magnesium chloride and lesser amounts of other materials.

The chemical treatment given to brines varies from plant to plant depending on impurities present. Typically, the brine may be first aerated to remove hydrogen sulfide and, in many cases, small amounts of chlorine are added to complete sulfide removal and oxidize all iron salts present to the ferric state. The brine is then pumped to settling tanks where it is treated with soda ash and caustic soda to remove most of the calcium, magnesium and iron present as insoluble salts. After clarification to remove these insolubles, the brine is then sent to multiple effect evaporators. As water is removed, salt crystals form and are removed as a slurry. After screening to remove lumps, the slurry is then washed with fresh brine. By this washing, fine crystals of calcium sulfate are removed from the mother liquor of the slurry and returned to the evaporator. Eventually the calcium sulfate concentration in the evaporator builds up to the point where it must be removed by "boiling out" the evaporators.

The washed slurry is filtered, the mother liquor is returned to the evaporators and the salt crystals from the filter are dried and screened. Salt produced from a typical brine will be of 99.8 percent purity or greater. Some plants do not treat the raw brine, but control the calcium and magnesium impurities by watching the concentrations in the evaporators and bleeding off

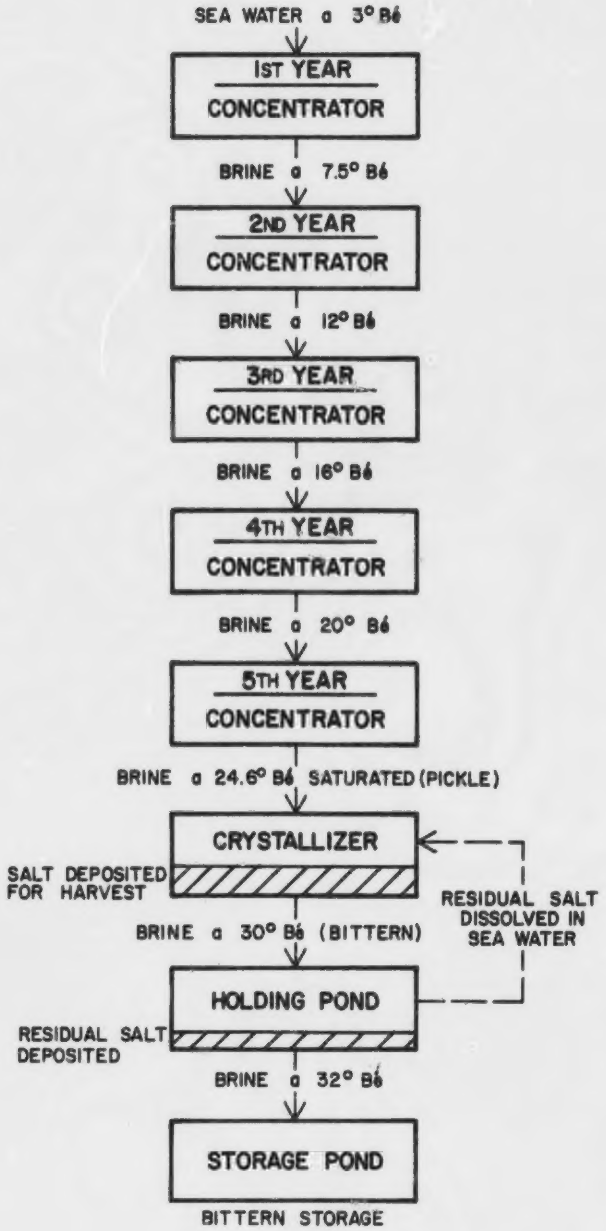

SEA WATER @ 3° Bé
1ST YEAR
CONCENTRATOR
BRINE @ 7.5° Bé
2ND YEAR
CONCENTRATOR
BRINE @ 12° Bé
3RD YEAR
CONCENTRATOR
BRINE @ 16° Bé
4TH YEAR
CONCENTRATOR
BRINE @ 20° Bé
5TH YEAR
CONCENTRATOR
BRINE @ 24.6° Bé SATURATED (PICKLE)
CRYSTALLIZER
SALT DEPOSITED FOR HARVEST
RESIDUAL SALT DISSOLVED IN SEA WATER
BRINE @ 30° Bé (BITTERN)
HOLDING POND
RESIDUAL SALT DEPOSITED
BRINE @ 32° Bé
STORAGE POND
BITTERN STORAGE

FIGURE 18
STANDARD SOLAR SALT PROCESS FLOW DIAGRAM

sufficient brine to maintain a predetermined level. By such methods, salt of better than 99.5 percent purity can be made.

In either case, the final screening of the dried salt yields various grades depending on particle size. A detailed process diagram is shown in Figure 19.

In the "Grainer" system, saturated and pretreated brine from the above processes is heated in a flat, open pan (or grainer). Flat crystals of sodium chloride form on the quiescent surface of the solution and fall to the bottom of the grainer. There they grow until they are removed by a submerged rake system. Recovered crystals are subsequently washed, dried, classified as to size, and packed. Brine pretreatment allows sodium chloride purities of 99.98 percent by this method.

In the "vacuum pan" system, pretreated brine enters vacuum evaporators which remove water and allow sodium chloride crystals to precipitate out. The crystals are then washed, filtered, and dried prior to packing. The "Alberger" process is similar except that an open evaporator is used to remove water sufficiently to allow precipitation of salt crystals. These crystals are centrifuged to remove liquid, dried, and packed. The feed to the open evaporator includes saturated brine and a slurry of sodium chloride crystals in brine. This slurry is the liquid effluent from the evaporator with some of the water removed by evaporation.

A wide variety of solid products are available, with various particle sizes, solid forms, purities, and additives. Exact production figures are not available, but current annual production appears to be between 40,000,000 and 50,000,000 kkg (44,000,000 and 55,000,000 tons). Because salt sources are widespread and the product is relatively inexpensive, production facilities are localized and operated on a relatively low profit margin. Major salt deposits in the U.S. include a large bed extending from western New York through much of Michigan, brine wells in the Ohio Valley, a large bed under central Kansas and northern Oklahoma, and salt domes in Texas and Louisiana. In 1971 salt production by solar evaporation was 2,140,000 kkg (2,350,000 tons) and the production by solution mining was 5,390,000 kkg (5,928,000 tons). Practically all chemical compounds containing sodium or chlorine are derived from salt. The chemical industry utilizes almost all of the brine produced and over half of the rock salt production. About three percent of the production is used as table salt, although more than this is utilized in the food processing industry.

Sodium Dichromate and Sodium Sulfate

Sodium dichromate ($Na_2Cr_2O_7$) is prepared by the calcination of a mixture of chrome ore (typically chromite, $FeO.Cr_2O_3$), sodium

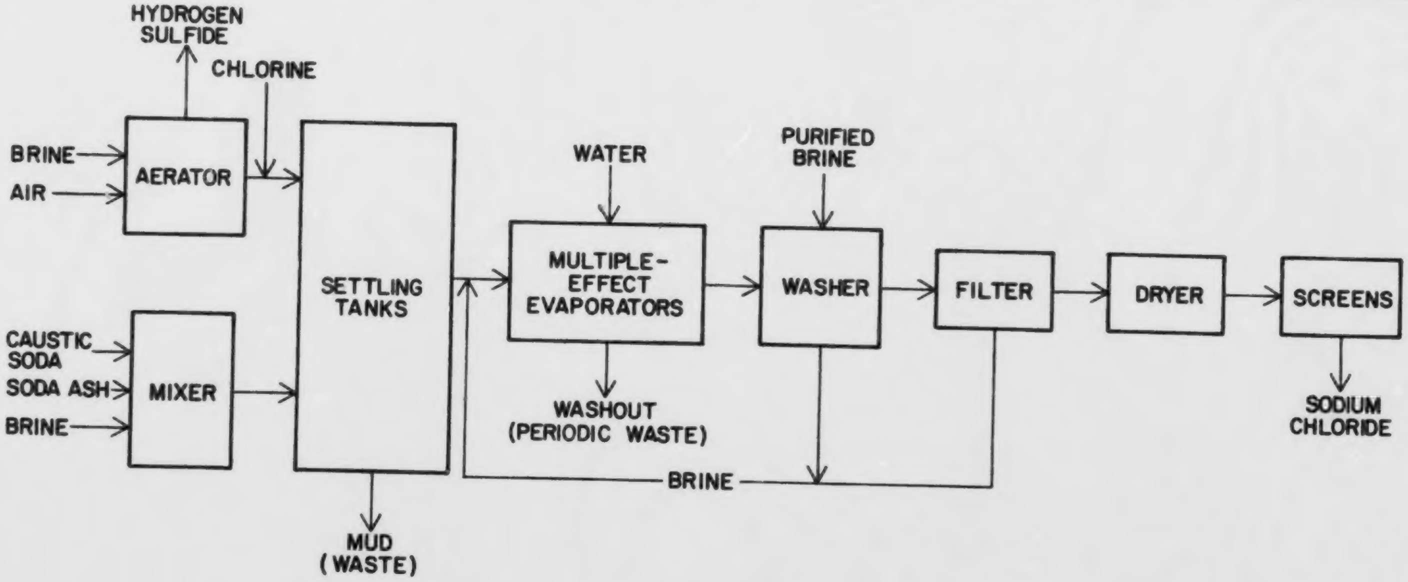

HYDROGEN SULFIDE
CHLORINE
BRINE
AIR
AERATOR
CAUSTIC SODA
SODA ASH
BRINE
MIXER
SETTLING TANKS
MUD (WASTE)
WATER
MULTIPLE-EFFECT EVAPORATORS
WASHOUT (PERIODIC WASTE)
PURIFIED BRINE
WASHER
FILTER
DRYER
SCREENS
SODIUM CHLORIDE
BRINE

FIGURE 12
STANDARD MULTIPLE-EFFECT EVAPORATION SODIUM CHLORIDE
PROCESS FLOW DIAGRAM

carbonate, and lime. This is followed by a water leach and conversion of the soluble chromates to dichromate with sulfuric acid, as shown in Figure 20. The overall reaction scheme is:

Formation of Chromate

$$4(FeO.Cr_2O_3) + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

Conversion to Dichromate

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + H_2O + Na_2SO_4$$

After the leaching operation, calcium salts are precipitated by pH adjustment and then removed along with the iron oxide. The leachate containing the soluble chromate is then acidified by addition of sulfuric acid, thereby forming the dichromate and sodium sulfate. The sulfate is removed and the dichromate solution is partially evaporated and removed to a crystallizer where sodium dichromate crystals are allowed to form. The crystals are centrifuged to remove excess water and then dried and packed for shipment.

Other chromate products are often made in the same plant, including production of "chromic acid" (sold as the liquid solution of CrO_3) by treatment of sodium dichromate with sulfuric acid, and sodium chromate, produced either by the chromite ore reaction above (crude chromate) or by reaction of sodium dichromate with soda ash (very pure product). Sodium dichromate is the major product of the industry. It is sold as an orange-colored dihydrate ($Na_2Cr_2O_7 \cdot 2H_2O$). Current production is estimated to be between 100,000 and 150,000 kkg (110,000 and 165,000 tons). The major demand for this chemical is in the manufacturing of pigments. Other uses include leather tanning, metal treatment, and corrosion inhibition.

Sodium sulfate (salt cake) is produced as a by-product from sodium dichromate manufacture, by direct mining and natural brine recovery operations, and as a by-product of organic syntheses. Most of the U.S. production arises from production of rayon and various organic chemicals and is not covered in this Document. Production from mining and natural brines is also not considered herein.

In sodium dichromate manufacture, soda ash, lime, and chrome ore are reacted as shown above. The products are then leached with sulfuric acid to convert the chromate to dichromate. The leachate, containing sodium sulfate in addition to sodium dichromate, is partially evaporated to the point where the sulfate is precipitated. The solid sulfate is filtered out, dried, and sold.

Since sodium sulfate is primarily a by-product material, the supply often exceeds the demand. In addition, the natural product is relatively abundant and limited in competition only by

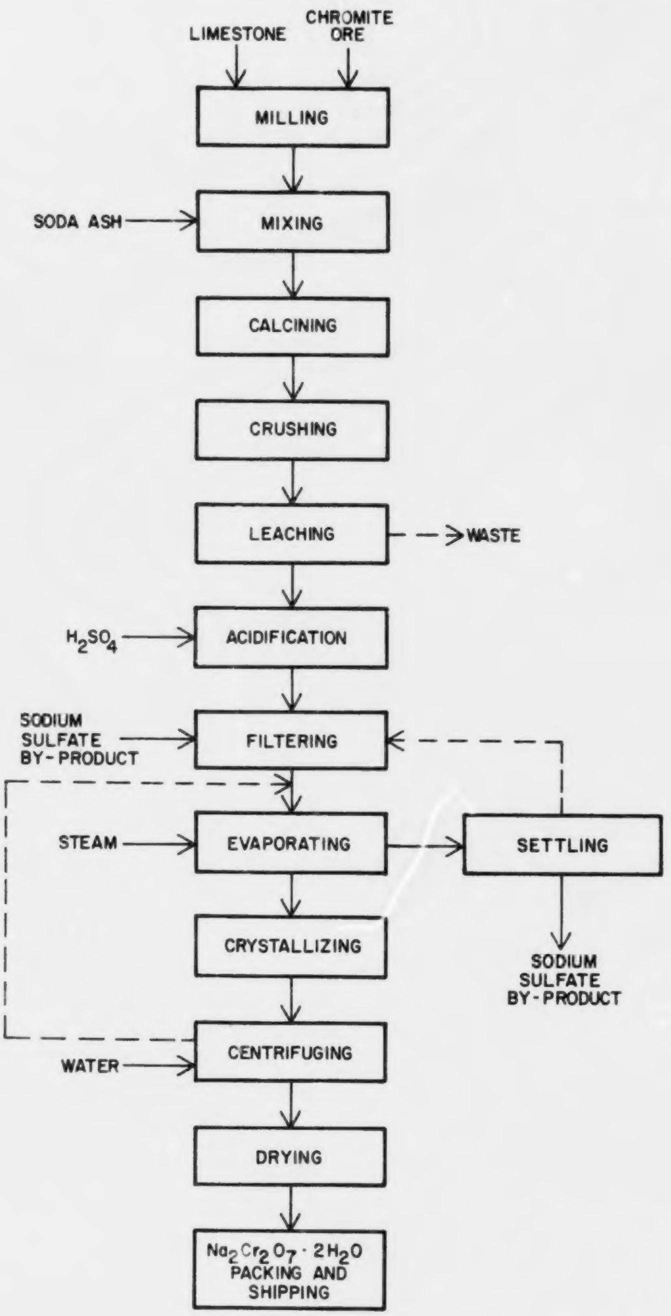

LIMESTONE
CHROMITE ORE
MILLING
SODA ASH
MIXING
CALCINING
CRUSHING
LEACHING
WASTE
H_2SO_4
ACIDIFICATION
SODIUM SULFATE BY-PRODUCT
FILTERING
STEAM
EVAPORATING
SETTLING
CRYSTALLIZING
SODIUM SULFATE BY-PRODUCT
WATER
CENTRIFUGING
DRYING
$Na_2Cr_2O_7 \cdot 2H_2O$ PACKING AND SHIPPING

FIGURE 20
STANDARD SODIUM DICHROMATE PROCESS DIAGRAM

distance from the markets. The largest use is in the kraft pulp and paper industry. Another major use is as a "builder" in detergents. Total U.S. production in 1971 was 764,409 kkg (842,788 tons) of high purity sodium sulfate and 465,785 kkg (513,545 tons) of Glauber's salt ($Na_2SO_4 \cdot 10H_2O$). The dichromate by-product is sometimes called "chrome cake". Present annual production of this form of sodium sulfate is estimated to be 110,000 kkg (121,000 tons).

Sodium Metal

Sodium metal is manufactured by electrolysis of fused (molten) sodium chloride at about 600°C (1072°F), as shown in Figure 21. The general equation is:

$$2NaCl + \text{direct current} \rightarrow 2Na + Cl_2$$

After purification to remove magnesium salts and sulfates, the sodium chloride is mixed with alkali fluorides and calcium chloride to lower the melting point. The charge is then fused in a "Downs" cell, which is a closed rectangular refractory-lined steel box with separate anode and cathode compartments separated by an inorganic diaphragm. The graphite or carbon anode is fed into the bottom of the cell, and the cathode is iron or copper in an annular form.

Molten sodium formed at the cathode is transported to a collection vessel. The metal is withdrawn from the bottom, filtered, and packaged in the form of bricks of various sizes. Very pure metal results from blanketing the cell and other processing equipment with argon gas to prevent oxygen from entering the system. Even the less pure product, because of its reactivity, must be protected from air and water throughout the production process. By-product chlorine is liberated in the cell, dried with sulfuric acid and the purified product is compressed and sold.

The U.S. production of sodium metal in 1971 was 138,839 kkg (153,075 tons). One of its major uses is in the manufacturing of tetraethyl lead and other organometallic compounds. Other uses include production of sodium cyanide, sodium peroxide, titanium, and zirconium. It is also used in liquid form as a nuclear reactor coolant and as a light, thermally-conductive solid in various applications.

Sodium Silicate

Several forms of sodium silicate are manufactured including both liquid and anhydrous (solid or powder) forms of sodium metasilicate (Na_2SiO_3), sodium orthosilicate (Na_4SiO_4), and sodium tetrasilicate ($Na_2Si_4O_9$). The liquid forms are generally sold in 20 - 50 percent by weight aqueous solutions called "water

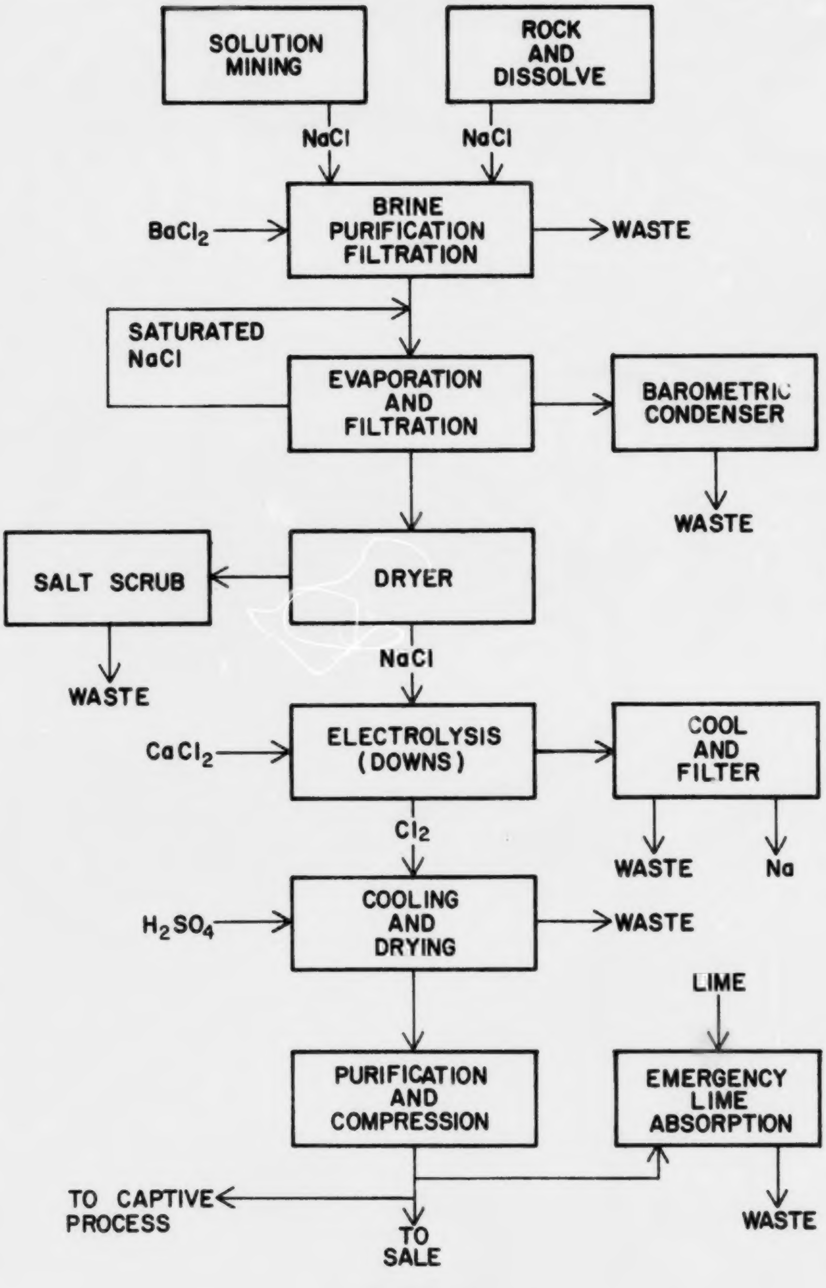

SOLUTION MINING
ROCK AND DISSOLVE
NaCl
NaCl
BaCl2
BRINE PURIFICATION FILTRATION
WASTE
SATURATED NaCl
EVAPORATION AND FILTRATION
BAROMETRIC CONDENSER
WASTE
SALT SCRUB
DRYER
WASTE
NaCl
CaCl2
ELECTROLYSIS (DOWNS)
COOL AND FILTER
Cl2
WASTE
Na
H2SO4
COOLING AND DRYING
WASTE
LIME
PURIFICATION AND COMPRESSION
EMERGENCY LIME ABSORPTION
TO CAPTIVE PROCESS
TO SALE
WASTE

FIGURE 21
STANDARD CHLORINE-SODIUM DOWNS CELL PROCESS FLOW DIAGRAM

glass", because they solidify to a glass which is water-soluble. The general production process as shown in Figures 22 and 23, involves reaction of caustic soda (NaOH) and silica (SiO_2). The relative proportions of the reactants determine the product composition. Equations for the several reactions are:

Sodium Metasilicate

$$4NaOH + 2SiO_2 + Heat \rightarrow 2Na_2SiO_3 + 2H_2O$$

Sodium Orthosilicate

$$4NaOH + SiO_2 + Heat \rightarrow Na_4SiO_4 + 2H_2O$$

Sodium Tetrasilicate

$$2NaOH + 4SiO_2 + Heat \rightarrow Na_2Si_4O_9 + H_2O$$

Sodium silicates, other than those listed above, can be produced by further variation of the caustic-silica reactant ratios.

In a typical process, caustic soda and silica sand are mixed in the desired proportion and charged to a furnace. Water and steam are added to the product under pressure to completely dissolve the silicate. The liquid product is then stored or used to produce silicate in solid form. The production of solid silicate from silicate solution essentially involves evaporation of the water, although the silicate in solution may be further reacted with a caustic solution during the process if a higher sodium crude content is desired in the solid product. This is typically the case in the production of sodium metasilicate (anhydrous) from tetrasilicate water glass. The dried anhydrous silicate is screened and milled to achieve the desired particle sizes.

Silicate plants are often captive to soap or catalyst manufacturers or other users. One of the major uses is in the manufacture of silica gel. In 1971, the U.S. production of sodium silicate in water glass form was 569,701 kkg (628,116 tons), and that of anhydrous sodium metasilicate was 244,808 kkg (269,910 tons).

Sodium Sulfite

The major process for sodium sulfite manufacture consists essentially of reacting sulfur dioxide with soda ash (Na_2CO_3). Another source is as a by-product from the production of phenol through the reaction of sodium benzene sulfonate with sodium hydroxide. The latter is not considered in this Document.

In the soda ash-sulfur dioxide reaction process, shown in Figure 24, the sulfur dioxide gas is passed into a solution of sodium carbonate until the product is acidic. At this point the solute consists primarily of sodium bisulfite ($NaHSO_3$), which is converted to sodium sulfite (Na_2SO_3) by the further addition of

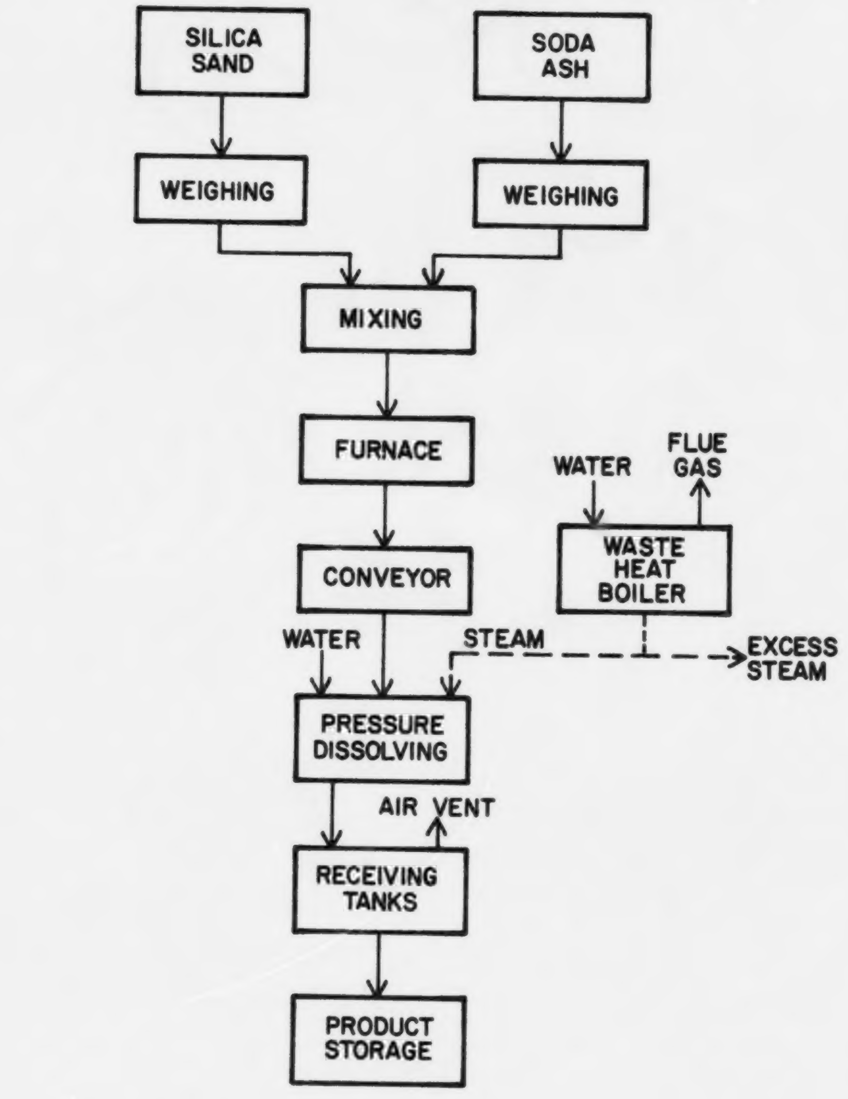

SILICA SAND
SODA ASH
WEIGHING
WEIGHING
MIXING
FURNACE
WATER
FLUE GAS
CONVEYOR
WASTE HEAT BOILER
WATER
STEAM
EXCESS STEAM
PRESSURE DISSOLVING
AIR VENT
RECEIVING TANKS
PRODUCT STORAGE

FIGURE 22
STANDARD LIQUID SODIUM SILICATE
FLOW DIAGRAM

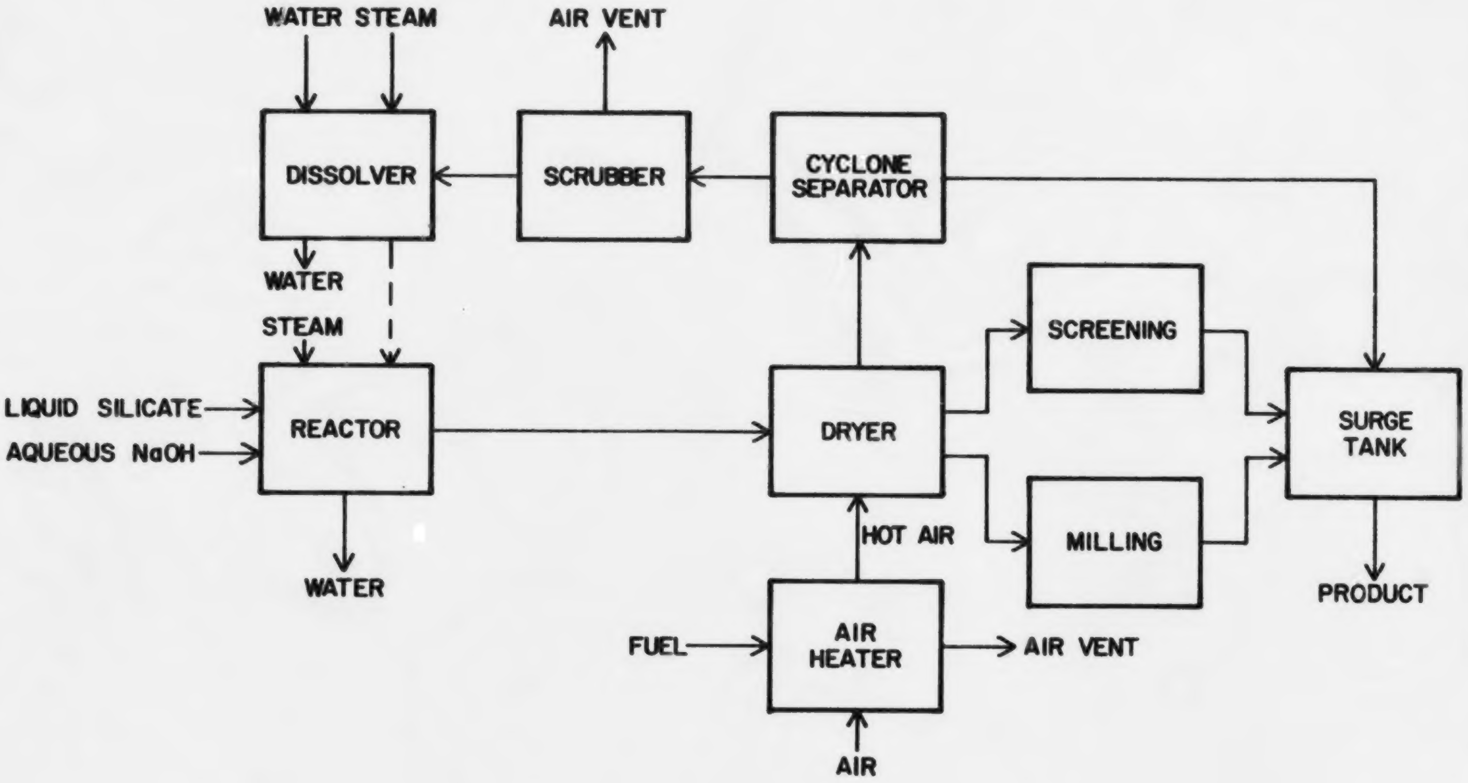

WATER STEAM
AIR VENT
DISSOLVER
SCRUBBER
CYCLONE SEPARATOR
WATER
STEAM
SCREENING
LIQUID SILICATE
AQUEOUS NaOH
REACTOR
DRYER
SURGE TANK
HOT AIR
MILLING
WATER
PRODUCT
FUEL
AIR HEATER
AIR VENT
AIR

FIGURE 23
STANDARD ANHYDROUS SODIUM METASILICATE FLOW DIAGRAM

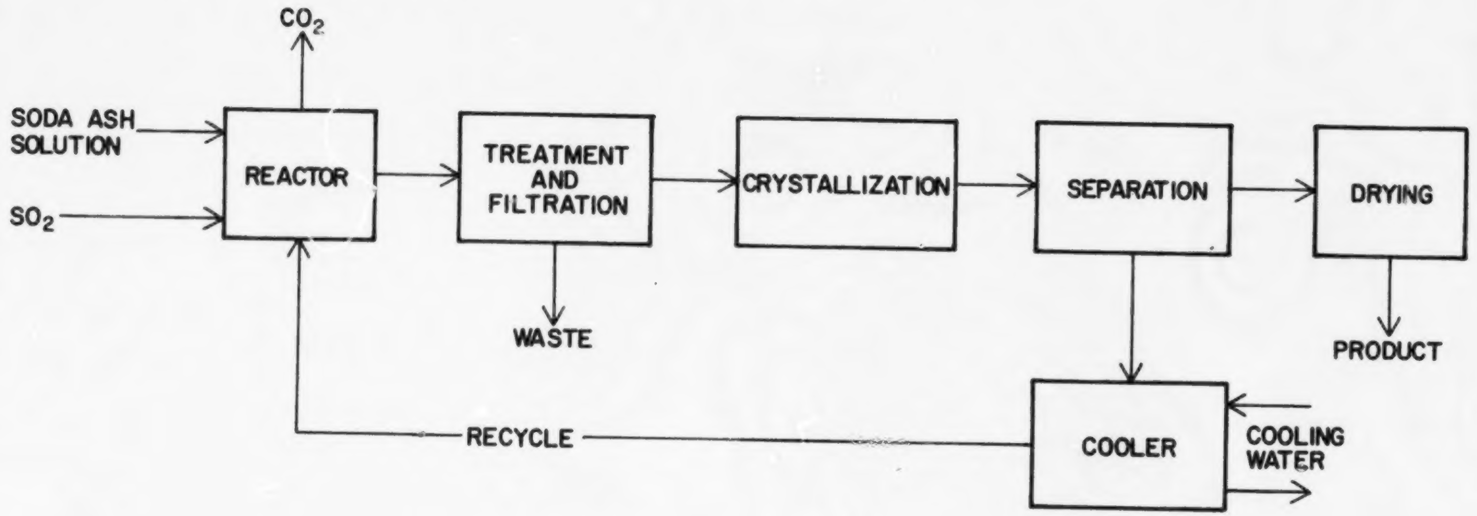

CO$_2$
SODA ASH SOLUTION
SO$_2$
REACTOR
TREATMENT AND FILTRATION
WASTE
CRYSTALLIZATION
SEPARATION
DRYING
PRODUCT
COOLER
COOLING WATER
RECYCLE

FIGURE 24
STANDARD SODIUM SULFITE PROCESS FLOW DIAGRAM

soda ash and heat until all the carbon dioxide is released. The overall reaction is:

$$SO_2 + Na_2CO_3 \rightarrow Na_2SO_3 + CO_2$$

The crude sulfate formed from this reaction is purified, filtered to remove insolubles from the purification steps, crystallized, dried and shipped.

Sodium sulfite is a mild reducing agent, and is widely used as an antioxidant. Specific uses include bleaching and stabilization of yarns, textiles and paper, preservation of foodstuffs and photographic developers, and as a boiler feed water additive. The paper industry is the largest consumer. Total U.S. production in 1971 was 185,393 kkg (204,402 tons).

Sulfuric Acid

Sulfuric acid is manufactured primarily by the contact process, which involves the burning of sulfur to sulfur dioxide, followed by the catalytic oxidation of sulfur dioxide to sulfur trioxide which is reacted with water to yield sulfuric acid. Using the contact process, are three types of plants:

(a) double absorption - paired sulfur trioxide absorption towers and catalyst beds in series are used to maximize conversion of sulfur dioxide so that tail gas scrubbers are not required;

(b) single absorption - single absorption towers and catalyst beds are used and tail gases frequently have to be scrubbed to remove sulfur oxides;

(c) spent acid plants - these plants use spent sulfuric acid in place of, or in addition to, sulfur as a raw material. While the acid production parts of these plants are the same as those for single absorption, these plants are unique because of the spent acid pyrolysis units used to convert the waste sulfur acid raw materials to a sulfur dioxide feed stream.

Almost all of the sulfuric acid production in this country arises from catalytic oxidation of sulfur dioxide to sulfur trioxide (SO_3) and its subsequent reaction with water to form the acid. The general reactions are:

$$2SO_2 + O_2 \rightarrow 2SO_3$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$

The source of the sulfur dioxide for acid manufacturing varies widely; raw materials include sulfur, refinery sludges, pyrites (sulfide ores), spent acid solutions, recovered SO_2, and by-product hydrogen sulfide. The sulfur, iron sulfide, and hydrogen sulfide are burned in air according to:

$$S + O_2 \rightarrow SO_2$$
$$4FeS_2 + 11O_2 \rightarrow 8SO_2 + 2Fe_2O_3$$
$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$

Sulfur dioxide from oxidation of iron sulfide or from roasting of other sulfide ores is relatively impure and requires removal of materials such as dust, moisture, arsenic, chlorine, and fluorine, all of which would poison the catalyst used in the contact process. Most of the U.S. production of sulfuric acid arises from the use of sulfur or refining sludge raw materials.

In the contact process, purified and dry sulfur dioxide is mixed with air, heated, and introduced into a reactor (converter) containing a platinum or vanadium pentoxide catalyst. The resulting gas mixture is cooled and sent to a succession of internally-cooled towers where the sulfur trioxide is absorbed by oleum (acid plus excess sulfur trioxide) of successively decreasing sulfur trioxide concentrations. Acid less than 97 percent concentration cannot be used to absorb sulfur trioxide because of mist formation and resulting sulfur trioxide losses. Various products are sold, ranging in acidic strength from battery acid (33.5 percent H_2SO_4, 50° Be) to 70 percent oleum (70 percent free SO_3 in H_2SO_4). Iron or steel containers can be used for the higher acid concentrations. Dilute acid requires specialized containers lined with glass, rubber, or lead.

In the double absorption contact process, sulfur is burned to yield dioxide which is then passed through a catalytic converter with air to produce sulfur trioxide. The sulfur trioxide is then absorbed in 95-97% sulfuric acid. The gases emerging from the absorber are then fed to a second converter to oxidize the remaining sulfur dioxide to sulfur trioxide which is then absorbed in a second absorption tower. The tail gases are vented to the atmosphere.

As in other versions of the contact process, 95-97 percent stream sulfuric acid is used in the absorption towers. Pickup of sulfur trioxide in this medium converts it to 98 percent acid. Some of this acid is drawn off for sale and the remainder is diluted back to 96-97 percent stream and recirculated through the absorption towers. A process flow diagram is given in Figure 25.

The single absorption process differs from that previously described only in the arrangement of the converters and absorbers. For the single absorption process, the sulfur dioxide is passed through one or more converters and then into one or more absorbers prior to venting to the atmosphere as shown in Figure 26. This arrangement is less effective for both conversion of sulfur dioxide to sulfur trioxide and for absorption of the sulfur trioxide into the absorber sulfuric acid. As a result, the tail gases may be scrubbed and this

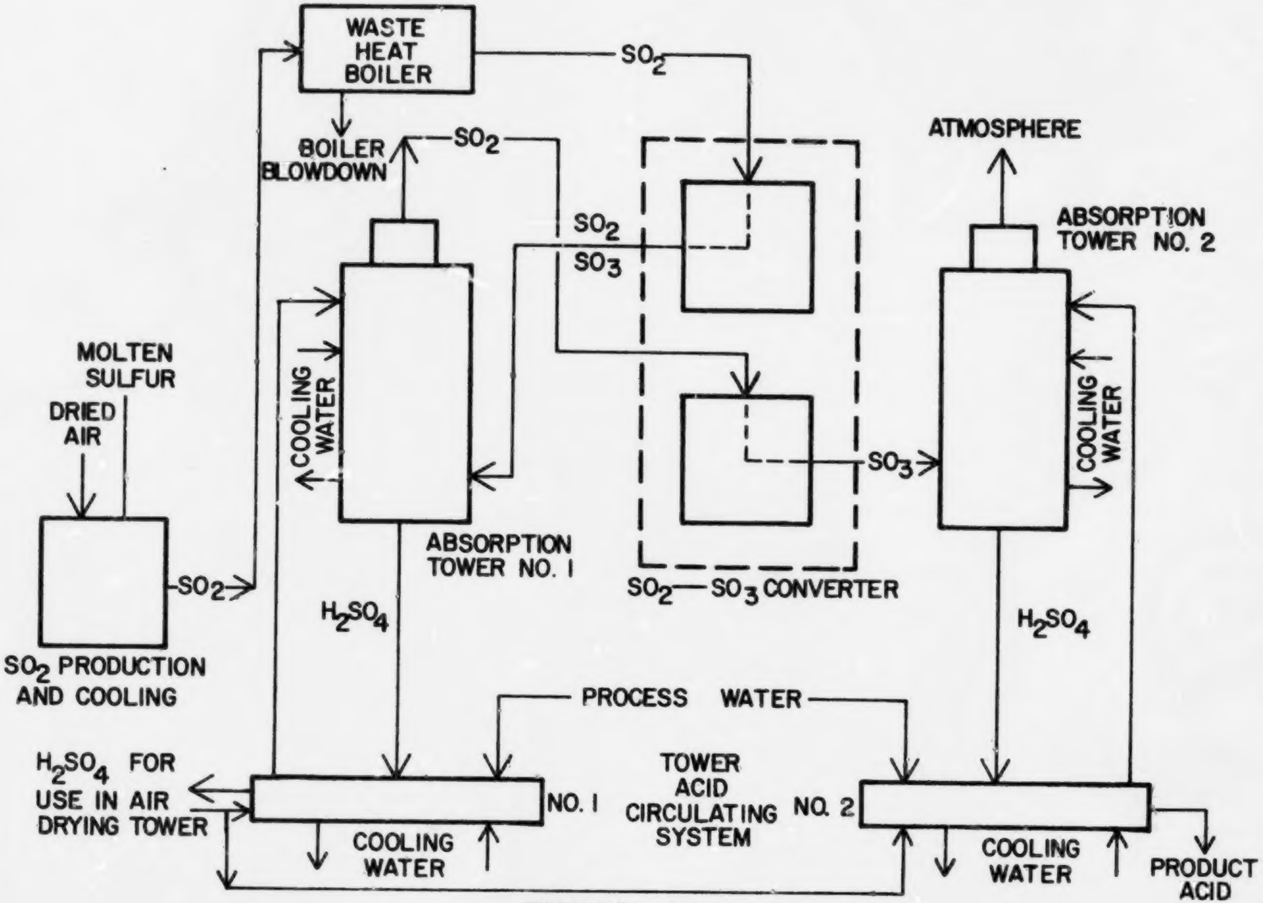

WASTE HEAT BOILER
SO_2
BOILER BLOWDOWN
SO_2
ATMOSPHERE
ABSORPTION TOWER NO. 2
SO_2
SO_3
MOLTEN SULFUR
DRIED AIR
COOLING WATER
SO_3
COOLING WATER
ABSORPTION TOWER NO. 1
SO_2
SO_2—SO_3 CONVERTER
H_2SO_4
H_2SO_4
SO_2 PRODUCTION AND COOLING
PROCESS WATER
H_2SO_4 FOR USE IN AIR DRYING TOWER
NO. 1
TOWER ACID CIRCULATING SYSTEM
NO. 2
COOLING WATER
COOLING WATER
PRODUCT ACID

FIGURE 25
SULFURIC ACID PLANT DOUBLE ABSORPTION

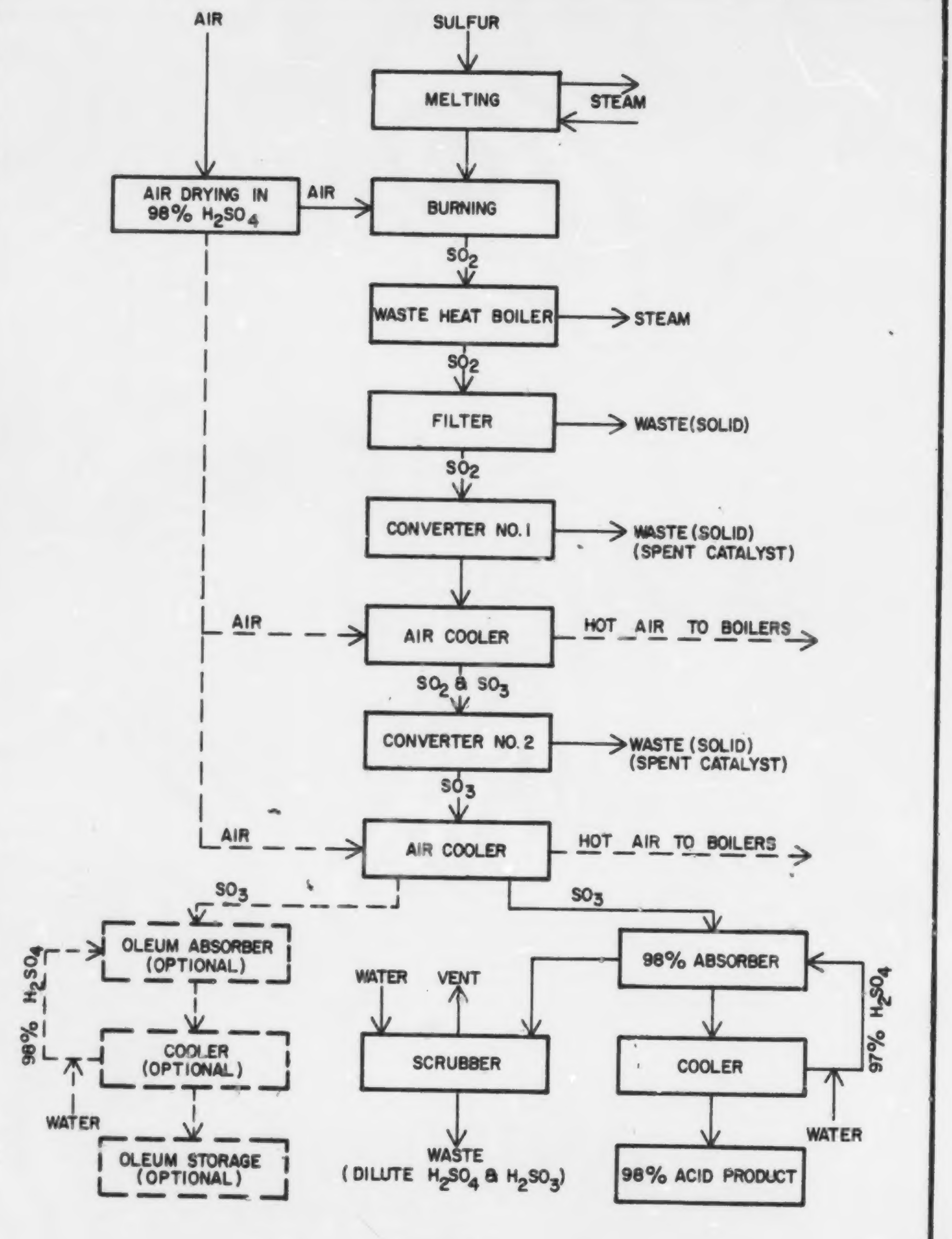

AIR
SULFUR
MELTING
STEAM
AIR DRYING IN 98% H_2SO_4
AIR
BURNING
SO_2
WASTE HEAT BOILER
STEAM
SO_2
FILTER
WASTE (SOLID)
SO_2
CONVERTER NO. 1
WASTE (SOLID) (SPENT CATALYST)
AIR
AIR COOLER
HOT AIR TO BOILERS
SO_2 & SO_3
CONVERTER NO. 2
WASTE (SOLID) (SPENT CATALYST)
SO_3
AIR
AIR COOLER
HOT AIR TO BOILERS
SO_3
SO_3
OLEUM ABSORBER (OPTIONAL)
98% H_2SO_4
COOLER (OPTIONAL)
WATER
OLEUM STORAGE (OPTIONAL)
WATER
VENT
SCRUBBER
WASTE (DILUTE H_2SO_4 & H_2SO_3)
98% ABSORBER
97% H_2SO_4
COOLER
WATER
98% ACID PRODUCT

FIGURE 26
STANDARD SULFURIC ACID SINGLE ABSORPTION FLOW DIAGRAM (CONTACT PROCESS)

creates a water-borne waste not present in double absorption plants.

Total U.S. production in 1971 was 26,685,916 kkg (29,422,179 tons). About 60 percent of this production is captive, much of it supplying the fertilizer, petroleum refining, and explosive industries. There are many other large-tonnage industrial uses, including the manufacture of synthetic plastics, detergents, hydrofluoric acid, nuclear fuels, and various other organic and inorganic chemical products.

Titanium Dioxide

Titanium dioxide is the most widely used white pigment. It is produced by two methods, the "sulfate" process and the "chloride" process.

a) Chloride process

In the chloride process, shown in Figure 27, titanium dioxide (TiO_2) ores are chlorinated to produce titanium tetrachloride. Coke is included to promote the reaction. The resulting titanium tetrachloride is oxidized to titanium dioxide and chlorine which is recycled. A general reaction scheme using rutile ($Fe_2O_3 \cdot TiO_2$) as the raw material is shown below:

Chlorination Reaction

$$TiO_2Fe_2O_3 + 2Cl_2 + C \quad TiCl_4 + CO_2 + FeCl_3$$

Oxidation Reaction

$$TiCl_4 + O_2 \longrightarrow TiO_2 + 2Cl_2$$

The chlorination reaction above is only approximate because the iron chloride which results may be a mixture of several chlorides, and some carbon monoxide is formed. The actual products and product ratios will depend on the composition of the raw material and the reactant ratios used.

Impurities in the system, including the iron and other metal (Al, V, etc.) chlorides, entrained coke and ore, carbon monoxide and dioxide, and hydrogen chloride all have to be removed prior to the oxidation reaction, creating a significant effluent waste control problem. After chlorination the products are cooled to condense the undesired metal chlorides. Solids are separated by centrifugation or filtration, and the gaseous titanium tetrachloride is condensed. Noncondensable reaction gases containing titanium tetrachloride, silicon tetrachloride and hydrogen chloride are water scrubbed, then vented. A number of techniques are used to further purify the tetrachloride, removing traces of silicon, vanadium, magnesium, manganese, aluminum, and chromium. These techniques include distillation, adsorption, ion exchange, and chemical precipitation with hydrogen sulfide,

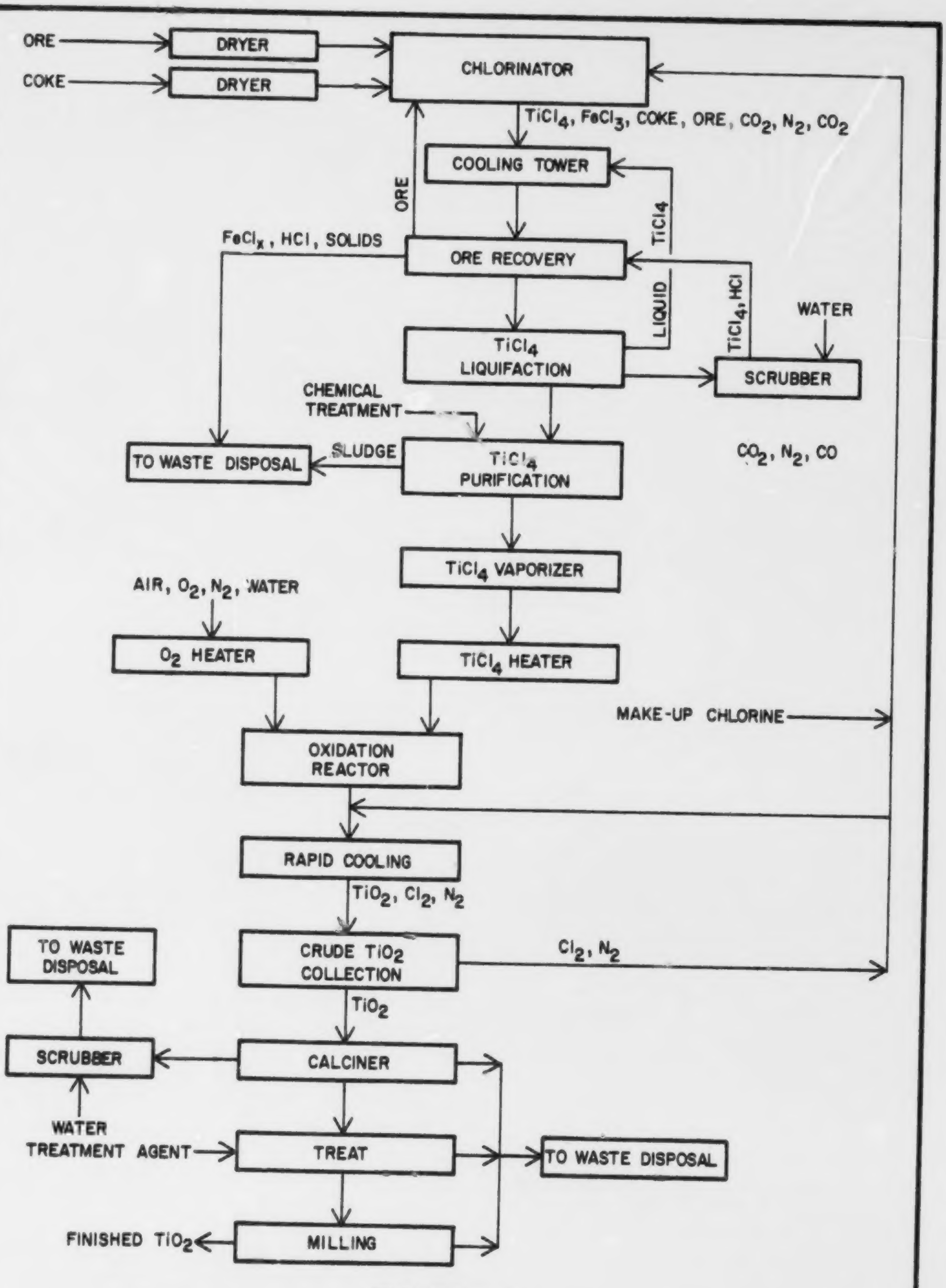

ORE
COKE
DRYER
DRYER
CHLORINATOR
TiCl4, FeCl3, COKE, ORE, CO2, N2, CO2
COOLING TOWER
ORE
TiCl4
FeClx, HCl, SOLIDS
ORE RECOVERY
LIQUID
TiCl4, HCl
WATER
TiCl4 LIQUIFACTION
SCRUBBER
CHEMICAL TREATMENT
TO WASTE DISPOSAL
SLUDGE
TiCl4 PURIFICATION
CO2, N2, CO
TiCl4 VAPORIZER
AIR, O2, N2, WATER
O2 HEATER
TiCl4 HEATER
MAKE-UP CHLORINE
OXIDATION REACTOR
RAPID COOLING
TiO2, Cl2, N2
TO WASTE DISPOSAL
CRUDE TiO2 COLLECTION
Cl2, N2
TiO2
SCRUBBER
CALCINER
WATER
TREATMENT AGENT
TREAT
TO WASTE DISPOSAL
FINISHED TiO2
MILLING

FIGURE 27
STANDARD CHLORIDE PROCESS TITANIUM DIOXIDE FLOW DIAGRAM

inorganic salts, or organic compounds. All techniques yield a pure titanium tetrachloride solution and a sludge which is slurried in water.

After purification, the titanium tetrachloride is vaporized and passed into a reactor with heated air or oxygen. The solid titanium dioxide particles are mechanically separated from the gas stream, calcined, ground, surface-treated, and packed.

b) Sulfate process

In the sulfate process, titanium dioxide-bearing ores are dissolved in sulfuric acid at high temperatures to produce titanium sulfate as an intermediate product. In some cases, small amounts of antimony trioxide are also added. The acid solution is clarified, a portion of the iron sulfates is removed by crystallization, and the titanium sulfate is hydrolyzed to form a white, non-pigmentary hydrate. The hydrate is calcined to form crystalline titanium dioxide, which is milled, surface treated, and packaged for sale. Product quality from the sulfate process is not so dependent on ore quality as is that from the chloride process.

A general reaction scheme using ilmenite containing various iron oxides (FeO and Fe_2O_3) is presented below:

Acidification

$$FeO(Fe_2O_3).TiO_2 + 5H_2SO_4 \rightarrow FeSO_4 + Fe_2(SO_4)_3 + TiOSO_4 + 5H_2O$$

Hydrolysis to Form Hydrate

$$TiOSO_4 + 2H_2O \rightarrow TiO_2.H_2O + H_2SO_4$$

Calcination

$$TiO_2.H_2O + Heat \longrightarrow TiO_2 + H_2O$$

After acidifications the solutions are clarified, cooled and sent to a vacuum crystallizer. There, ferrous sulfate crystallizes out and is separated from the mother liquor by centrifugation. This material is either sold or disposed of as a waste.

The mother liquor is clarified by filtration after addition of filter aids and further concentrated by vacuum evaporation. Seed crystals or other nucleating agents are added and the concentrated liquor is treated with steam to hydrolyze the titanyl sulfate present. This precipitates as acidic hydrated titanium. The precipitate is collected by filtration, washed several times and calcined at 900-950°C to yield titanium dioxide. This calcined product is ground, and further processed to yield a purer product. A standard process flow diagram is given in Figure 28.

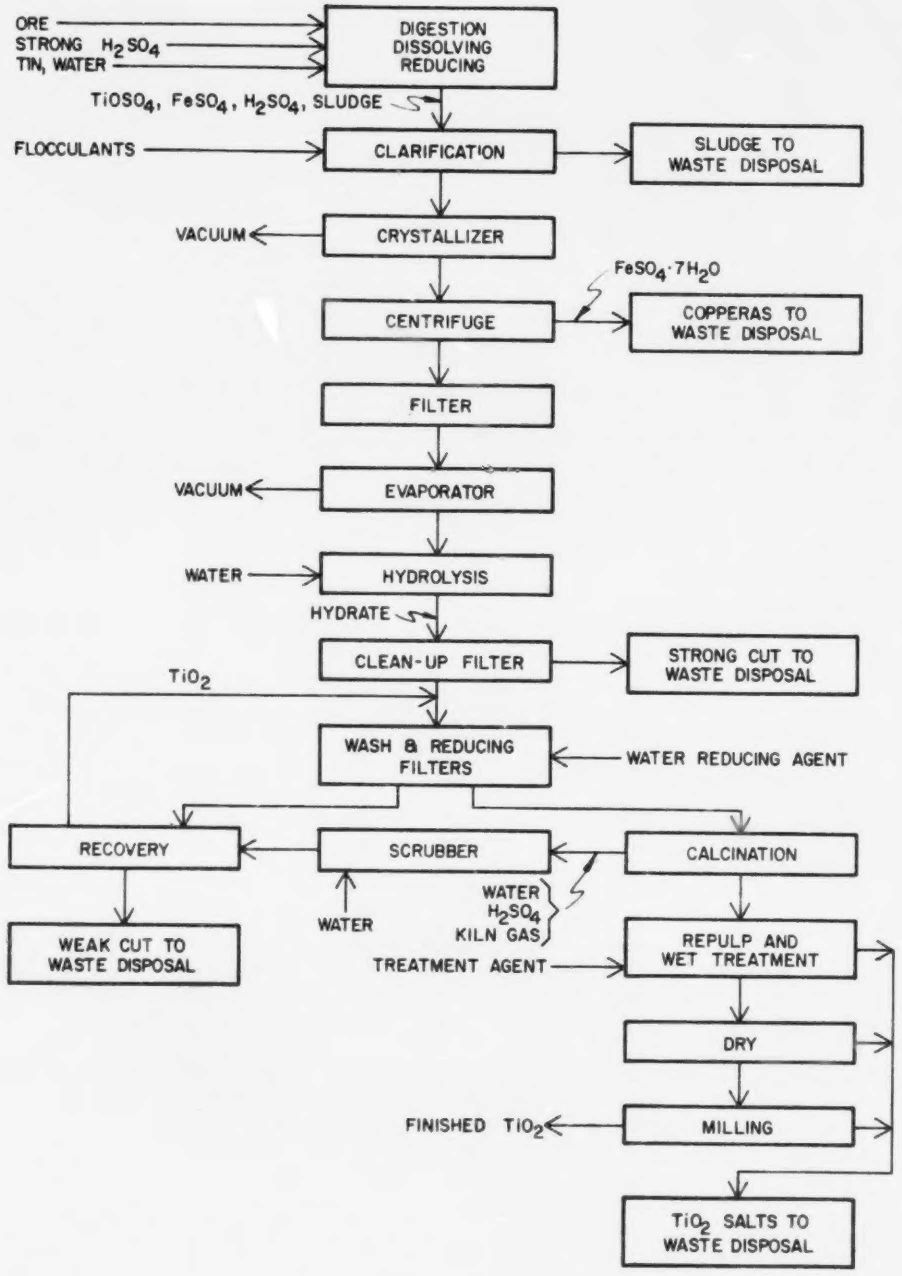

ORE
STRONG H_2SO_4
TIN, WATER
DIGESTION DISSOLVING REDUCING
$TiOSO_4$, $FeSO_4$, H_2SO_4, SLUDGE
FLOCCULANTS
CLARIFICATION
SLUDGE TO WASTE DISPOSAL
VACUUM
CRYSTALLIZER
$FeSO_4 \cdot 7H_2O$
CENTRIFUGE
COPPERAS TO WASTE DISPOSAL
FILTER
VACUUM
EVAPORATOR
WATER
HYDROLYSIS
HYDRATE
CLEAN-UP FILTER
STRONG CUT TO WASTE DISPOSAL
TiO_2
WASH & REDUCING FILTERS
WATER REDUCING AGENT
RECOVERY
SCRUBBER
CALCINATION
WATER
H_2SO_4
KILN GAS
WATER
WEAK CUT TO WASTE DISPOSAL
TREATMENT AGENT
REPULP AND WET TREATMENT
DRY
FINISHED TiO_2
MILLING
TiO_2 SALTS TO WASTE DISPOSAL

FIGURE 28
STANDARD SULFATE PROCESS TITANIUM DIOXIDE FLOW DIAGRAM

Various grades, purities, and surface finishes of several crystalline forms are sold commercially. Although the paint industry is the major user, various types of titanium dioxide are used in paper, inks, fabrics, rubber, and floor coverings. Total U.S. production in 1971 was 614,720 kkg (677,751 tons). Domestic ore is found in New York and Florida, plus lesser amounts in North Carolina, Virginia, and Idaho. The remaining ore supply is imported, much of it from Canada and India. Most of the production of this pigment is captive to the large paint manufacturers.

SECTION IV

INDUSTRY CATEGORIZATION

For the purpose of establishing effluent limitation guidelines for existing point sources and standards of performance for new sources, the inorganic chemicals manufacturing category has been segmented into subcategories based on the specific inorganic product manufactured. In cases where one chemical is produced by dissimilar processes, the product subcategory has been further subdivided. Although similar waste water constituents may be generated from various product groupings, as shown in Figure 29, and may be treated to similar concentrations, water requirements are specific for each chemical manufacturing process. Guidelines based on production volume must reflect this difference.

The separation of each product into individual subcategories simplifies the application of the effluent guidelines and standards of performance by providing unambiguous direction as to the application of a standard to a given point source. This is critical because of the great variety of product mix in existing facilities. The substantial advantage of clarity outweighs any technical advantages of product grouping.

In developing effluent limitations and standards of performance, it was necessary to examine numerous factors to determine whether additional segmentation of the industry is justified. The factors considered include:

(a) Waste water constituents
(b) Treatability of waste waters
(c) Manufacturing process
(d) Plant age
(e) Plant size
(f) Product mix
(g) Raw materials
(h) Air pollution control devices
(i) Geographical location.

A summary of the rationale employed in determining whether these factors necessitate further subcategorization is presented below.

(a) Waste water constituents.

The selected subcategorization scheme reflects gross differences in the raw waste loads generated from different chemical manufacturing processes. While it is recognized that the character and quantities of waste water pollutants may vary within a product subcategory, this difference is not sufficient to justify additional segmentation. When two different processes

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used to manufacture the same chemical generate dissimilar waste water constituents, they have been considered individually.

(b) Treatability of waste waters.

The treatability of waste water is determined largely by the volume of waste water and by the type of pollutants present. Thus, the above discussion on waste water constituents is applicable here.

(c) Manufacturing process.

Establishing subcategories based on product manufactured generally reflects differences between various manufacturing processes. The product subcategories are further segmented if two dissimilar manufacturing processes are commonly used.

(d) Plant age.

The relative age of plants within a product subcategory are determined by obsolesence due to process or equipment changes and not physical age. Hence, plant age is not an appropriate basis for subcategorization. No correlation between plant age and effluent quality is evident from plant data.

(e) Plant size.

Plant size generally has little effect on the quality of waste water generated from various chemical manufacturing processes. Although treatment costs per unit of production are somewhat lower when large quantities of water are treated, this difference is not sufficiently great to warrant further segmentation of the industry.

(f) Product mix.

Chemical plants vary greatly in terms of the number and types of products manufactured. More treatment options and a greater reuse potential exist in plants manufacturing many chemicals. However, treatment alternatives exist for small and single-product plants, such that additional subcategorization is unnecessary.

(g) Raw materials

Different raw materials are obviously used to manufacture different products. This difference is reflected in the selected subcategorization scheme. However, within a product subcategory raw materials of varying degrees of purity are used. Because ore beneficiation and cleaning may be used to treat impure ores, raw material quality does not justify further segmentation of the industry. In certain cases different raw materials do not alter the treatability of the process effluent. This is demonstrated in aluminum sulfate production where bauxite or aluminum clays are used as the source of aluminum.

(h) Air pollution control devices.

The type of system used to control air pollution will have an effect on the water treatment requirements of a given plant. Wet scrubbing solutions are the only source of waste water in some chemical manufacturing processes. In general, scrubbing solutions may be treated and recycled or reused. In some cases, this solution may be sold as a weak product solution. Product recovery justifies conversion to a dry bag collection system for some manufacturing processes. Because of the options available to economically treat, sell, recycle, reuse or eliminate scrubbing solutions, it was considered unnecessary to subcategorize according to methods of air pollution control.

(i) Geographical location.

Geographical location is important in analyzing the feasibility of various treatment alternatives. Evaporation ponds are functional only in areas where net evaporation exceeds rainfall. Ocean dumping and deep-well disposal are possible only in certain areas, and must be consistent with local, State and Federal laws. The possibility of ground water contamination may preclude the use of unlined holding and settling ponds in many locations. The location of a plant, therefore, is an important factor in selecting the appropriate treatment technologies for a specific plant. Because alternative treatment systems are available to accommodate differences in climate, geology, etc., additional subcategorization based on plant location is not justified. Allowances have been provided to permit discharges from impoundment in locations where rainfall exceeds evaporation.

The product subcategories are shown below with process subdivisions where required:

Aluminum chloride
Aluminum sulfate
Calcium carbide
Calcium chloride
Calcium oxide and calcium hydroxide
Chlorine and sodium or potassium hydroxide
    a. mercury cell process
    b. diaphragm cell process
Hydrochloric acid
Hydrofluoric acid
Hydrogen peroxide
    a. electrolytic process
    b. organic process
Nitric acid

- Potassium metal
- Potassium dichromate and potassium sulfate
- Sodium bicarbonate
- Sodium carbonate
- Sodium chloride
  - a. brine-mining process
  - b. solar evaporation process
- Sodium dichromate and sodium sulfate
- Sodium metal
- Sodium silicate
- Sodium sulfite
- Sulfuric acid
- Titanium dioxide
  - a. chloride process
  - b. sulfate process.

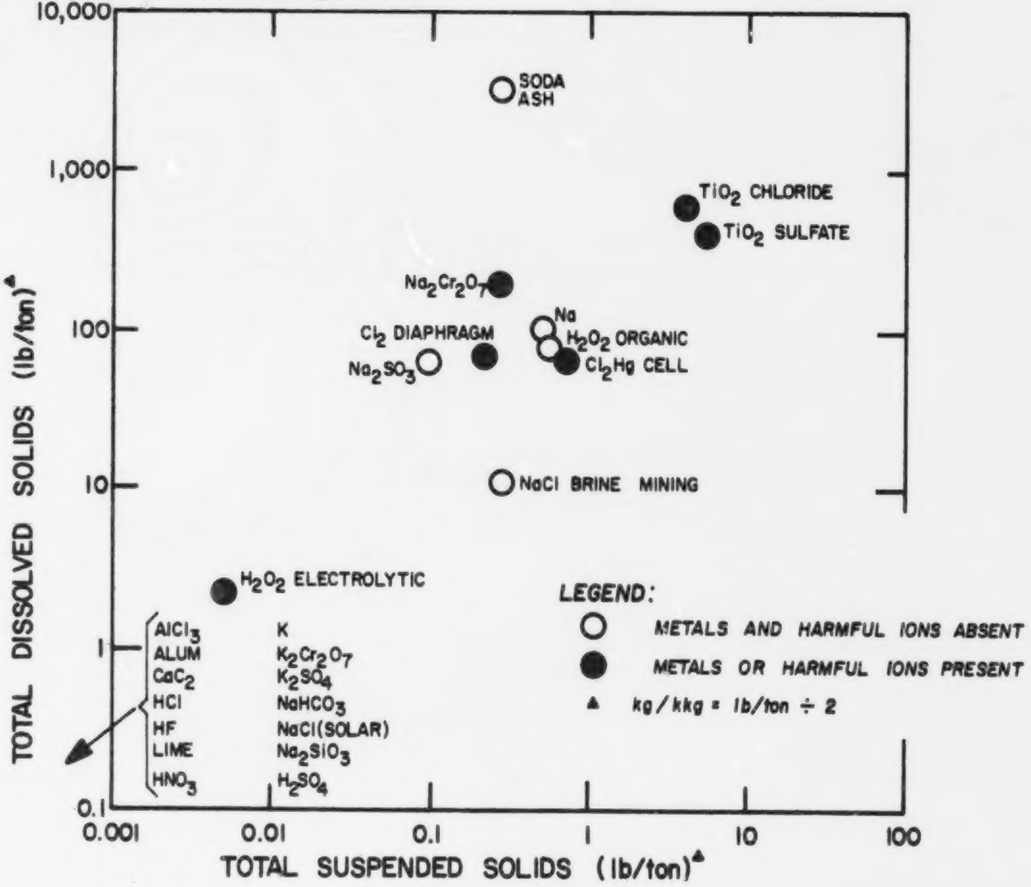

FIGURE 29
INDUSTRY CATEGORIZATION OF
INORGANIC CHEMICALS MANUFACTURING

SECTION V

WATER USE AND WASTE CHARACTERIZATION

This section discusses the specific water uses required in the manufacturing processes for the inorganic chemicals studied, and the amounts of waste effluents contained in these waters. The process wastes are characterized as raw waste loads emanating from a typical process before treatment and the amount of water-borne waste effluent after treatment. Also included in this discussion are verification sampling data measured at specific plants for each of the chemical subcategories set forth in Section IV. A description of the analytical techniques used for this verification of plant data is also provided.

GENERAL WATER USES

Water is used in inorganic chemical manufacturing plants for six principal purposes, plus other miscellaneous uses. The principal uses are:

1) Cooling -- Non-contact cooling water
2) Process -- Contact cooling or heating water
   Contact wash water
   Transport water
   Product and dilution water
3) Auxiliary water

The effluent guidelines developed in the document are to be applied to process waste water pollutants only. This includes those waste water constituents in water which directly contacts the product, by product, intermediate, raw material, or waste product. The guidelines do not include noncontact cooling water, or wastes resulting from steam or water supply. Guidelines for these waste streams will be developed in a separate study at a later date.

Non-Contact Cooling Water

Many chemical processes operate more quickly or more efficiently at high temperatures or generate heat. Cooling water is often used to control or reduce these temperatures. If the water is used without contacting the reactants, such as in a tube-in-shell heat exchanger or trombone cooler, then the water will not be contaminated with process effluent. If, however, the water contacts the reactants, then contamination of the water results and the waste load increases.

The non-contact cooling water in the industry is of two types. The first type is recycled cooling water which is cooled by cooling towers or spray ponds. The second type is once-through cooling water whose source is generally a river, lake or tidal estuary, and this water is usually returned to its source.

The only waste effluent from recycled water would be water treatment chemicals and the cooling tower blowdown which generally is discharged with the cooling water. The only waste effluent from the once-through cooling water would be water treatment chemicals which are generally discharged with the cooling water. The cooling water tower blowdown may contain phosphates, nitrates, nitrites, sulfates and chromates. The water treatment chemicals may consist of alum, hydrated lime, or alkali metal ions (sodium or potassium) arising from ion exchange processes. Regeneration of the ion exchange units is generally accomplished with sodium chloride or sulfuric acid, depending upon the type of unit employed.

Contact Cooling or Heating Water

This water comes under the general heading of process water because it comes into direct contact with process reactants. This type of water is used by steam drum dryers and barometric condensers. Water is required in very large quantities for use in the barometric condensers used to provide reduced pressure for the operation of multiple effect evaporators. For a large triple-effect evaporator, such as that used for salt evaporation, flows of 3,800-41,600 cu m/day (1 to 11 million gallons per day) are not unusual. A waste effluent problem with the barometric condenser usage arises from the product vapors and carry-over from the last effect (stage) of the evaporator which are entrapped in the flow of condenser water.

Other direct contact cooling or heating water usage such as that for contact steam drying, steam distillation, pump and furnace seals, etc., is generally of much lower volume than the barometric condenser water.

Contact Wash Water

This water is considered process water because it comes into direct contact with either the raw material, reactants or products. Examples of this type of water usage are ore washing to remove fines, filter cake washing to remove entrained particles, cleansing of insoluble product vapors, and absorption processes wherein water is reacted with a gaseous material to produce an aqueous solution.

Transport Water

Water is often used in the inorganic chemicals manufacturing industry for transporting reactants or products to various unit operations either in solution, suspension or slurry form. A good example of this is solution-mined salt or brine. Water is pumped into a salt cavity at the rate of 3900 l/kkg (936 gal/ton) of salt. The salt is dissolved, and the resulting brine is forced to the surface under pressure where it can be fed to evaporators to produce dry salt, or fed to electrolytic cells where it is used to produce chlorine and alkali. Wastes resulting from these types of operations are generally dilute solutions or suspensions which could be reused upon concentration or could be returned to the source. In cases where transport water is carrying a solid product, it normally is separated from the product by filtration, evaporation, or drying. The resultant liquor or condensate generally contains dissolved product, reactants or impurities.

Product Water

The product water generally is that which comes in contact with and becomes an integral part of the product. Typical examples include digestion water used for sodium silicate manufacture and water used in acid absorption towers. Likewise, water may be added to a highly concentrated product to form a more dilute product. The source of these waters is generally fresh water supplies, steam condensate, dilute product streams, or a combination of these sources.

Auxiliary Process Water

This water is used for auxiliary operations such as ion exchange regenerants, make-up water to cooling towers with a resultant cooling tower blowdown, make-up water to boilers with a resultant boiler blowdown, and storage and shipping tank washing. The water effluents from these operations are generally low in quantity but highly concentrated in waste materials.

Miscellaneous Water Uses

These water uses vary widely among the plants with general usage for floor washing and cleanup, safety showers and eye wash stations, sanitary uses, and storm run-off. The resultant streams are either not contaminated or only slightly contaminated with wastes. In instances where process residues collect where they can be washed away by storm waters, as for example, dusts on the exterior of process buildings, storm run-off can constitute a serious contamination problem.

PROCESS WASTE CHARACTERIZATION

Aluminum Chloride

Aluminum chloride is made by reaction of chlorine with molten aluminum. The aluminum chloride formed vaporizes and is collected on air cooled condensers. The tail gases leaving the condensers are the only source of wastes downstream of the reaction zone. Plant 125 is the exemplary plant for this production process. Figure 30 shows a scrubber system for this plant.

In the process described above, there are two sources of waste-uncondensed aluminum chloride and chlorine in tail gases and unreacted aluminum metal. At the exemplary facility, the first waste is utilized to manufacture another product and the unreacted aluminum is disposed of as a solid waste.

The raw waste loads are shown below:

Waste Product	Source	kg/kkg of Product (lb/ton) Average	Range
$AlCl_3$	Tail Gases	80 (160)	64-96 (128-192)
Unreacted Aluminum	Reactor	22 (44)	

At the exemplary plant there is an integrated blower system to exhaust the plant, packing station, condensers, etc. All blower exhaust is treated in an absorption tower where, as shown in Figure 30, the aluminum chloride and chlorine vapors are absorbed into a recycling scrubber system. From this scrubber, about 121 l of solution/kkg of product (29 gal/ton) are drawn off, filtered and further treated to produce a 28 percent aluminum chloride solution which is sold. There are no waste streams. The water input and use for the scrubber system is an equivalent volume. This water is supplied from a well for makeup to the system. None of this is recycled. It is used to make 28 percent solution product.

The characteristics of the 28 percent aluminum chloride solution recovered for sale are tabulated below:

Aluminum Chloride Solution
ACS-0002
Technical Grade

$AlCl_3$ percent	28 min.
Baume' at 15°C	32° min.
Total aluminum as aluminum oxide, percent	10.5 min.
Color, APHA	100 max.
Free Aluminum, percent	0.1 max.
Fe	25 mg/l

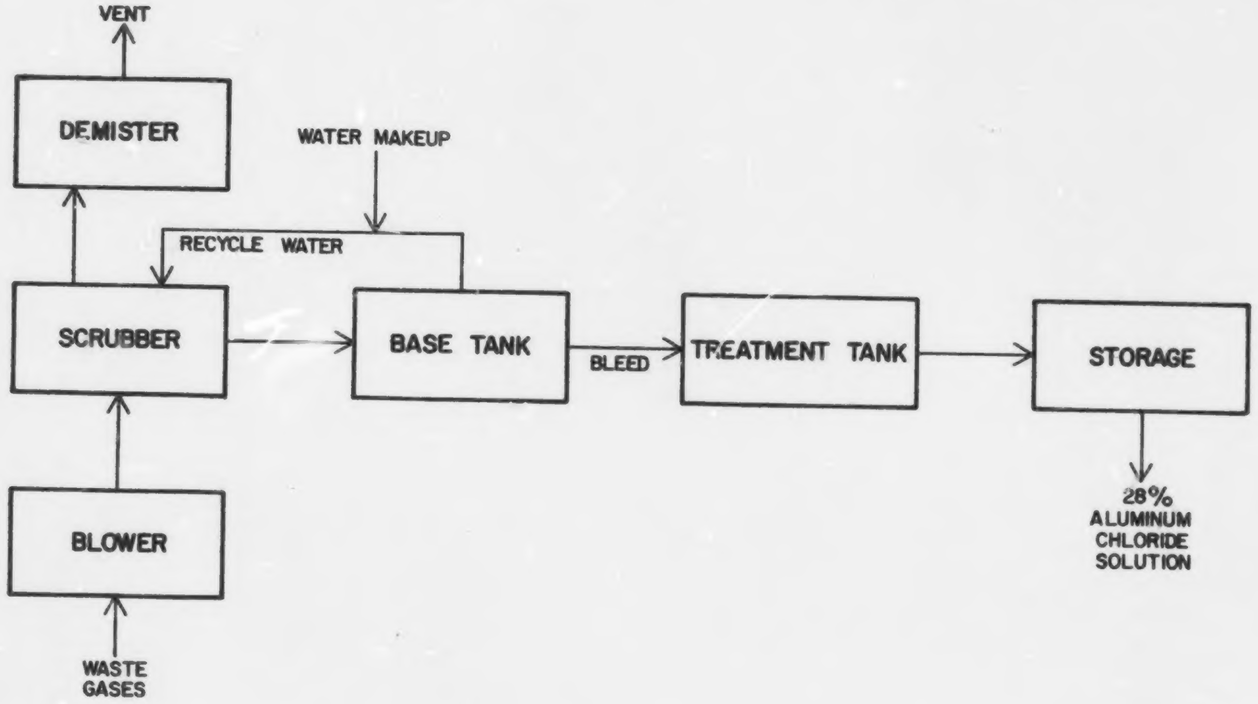
VENT
DEMISTER
WATER MAKEUP
RECYCLE WATER
SCRUBBER
BASE TANK
BLEED
TREATMENT TANK
STORAGE
BLOWER
WASTE GASES
28% ALUMINUM CHLORIDE SOLUTION

FIGURE 30
SCRUBBER SYSTEM FOR TREATMENT OF ALUMINUM CHLORIDE WASTES AT PLANT 125

Heavy metals	10 mg/l
Sulfate	500 mg/l
Free Acidity as percent HCl	0.2 max.
Freezing point	-34 (-30)
Density at 15°C, g/cc (lb/gal)	1.28 (10.7)

There are three types of aluminum chloride manufactured, all from the same process:

1. Yellow -- this product is made using a slight excess of chloride (0.0005 percent) and may contain some iron due to reaction of the chlorine with the vessel.
2. White -- this product has a stoichiometric aluminum/chloride ratio.
3. Grey -- this product contains 0.01 percent excess aluminum. The unreacted aluminum raw waste load is higher for the grey material.

Industrially, it generally makes little difference which of the above grades is employed. In some pigment and dye intermediate applications, however, the yellow material is preferred as it is free of elemental aluminum.

Aluminum Sulfate

Aluminum sulfate is prepared by reaction of bauxite ore or aluminum clays with sulfuric acid. The ore and sulfuric acid are reacted in a digester and the resulting aluminum sulfate solution, containing muds and other insolubles from the ore, is then fed to a settling tank, wherein the insolubles are removed by settling and filtration. The filtered product liquor is either shipped as liquid aluminum sulfate solution or evaporated to recover a solid product. Two exemplary plants for this product were studied, plants 049 and 063. Figure 31 shows a detailed process diagram including waste treatment for one plant, and Figure 32 is a similar diagram for the other.

Raw wastes from the process include insoluble muds from the digester, settling tank and filtration unit, as well as washwaters from vessel cleanouts. At one facility, these wastes are treated in a settling basin to remove the muds and the supernatant is reused in the process. A similar recycling system is used in the other facility.

Raw wastes from aluminum sulfate manufacture are listed below:

Waste Products	Process Source	kg/kkg of Product (lb/ton)	
Spent aluminum sulfate muds	Mud washing	170 (340) 100 (200)	(two different facilities)
Low aluminum sulfate water	Mud washing	800 (1600)	

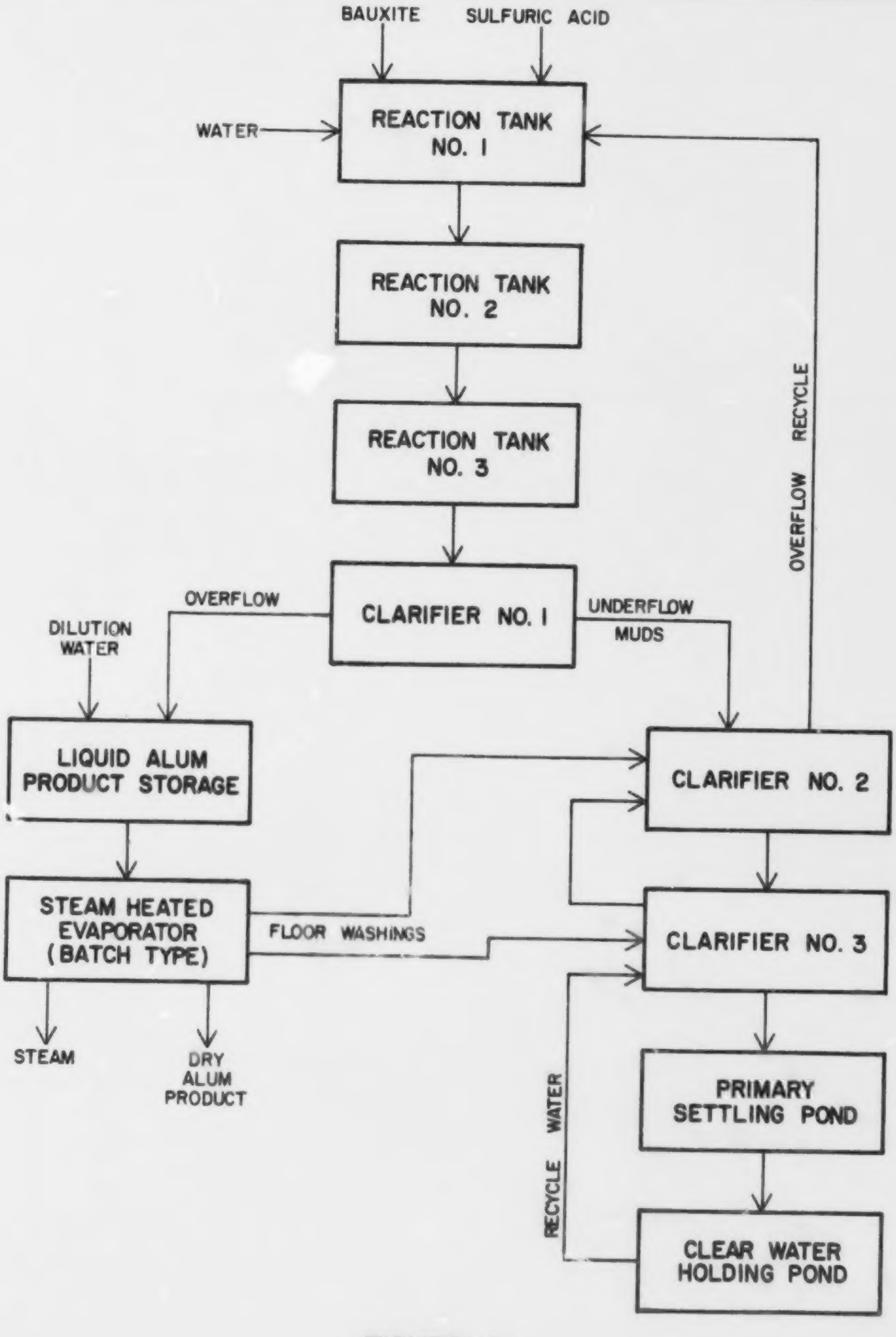
BAUXITE
SULFURIC ACID
WATER
REACTION TANK NO. 1
REACTION TANK NO. 2
REACTION TANK NO. 3
CLARIFIER NO. 1
OVERFLOW
UNDERFLOW MUDS
DILUTION WATER
OVERFLOW RECYCLE
LIQUID ALUM PRODUCT STORAGE
STEAM HEATED EVAPORATOR (BATCH TYPE)
FLOOR WASHINGS
STEAM
DRY ALUM PRODUCT
CLARIFIER NO. 2
CLARIFIER NO. 3
PRIMARY SETTLING POND
CLEAR WATER HOLDING POND
RECYCLE WATER

FIGURE 31
ALUMINUM SULFATE PROCESS AND TREATMENT FLOW DIAGRAM AT PLANT 063

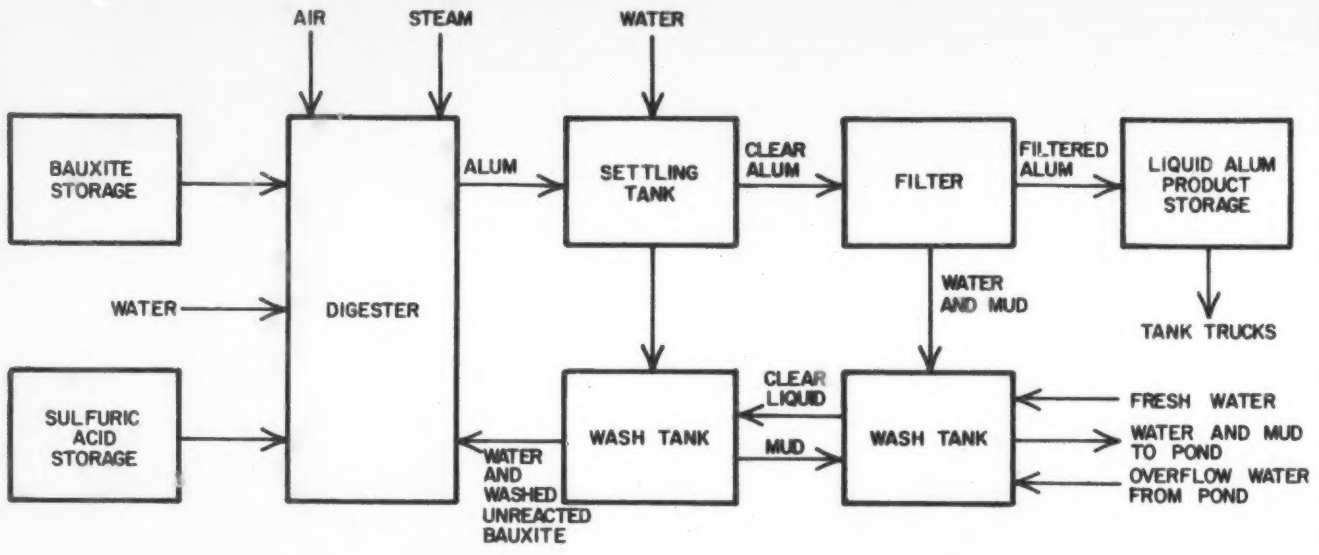
AIR
STEAM
WATER
BAUXITE STORAGE
DIGESTER
ALUM
SETTLING TANK
CLEAR ALUM
FILTER
FILTERED ALUM
LIQUID ALUM PRODUCT STORAGE
WATER
WATER AND MUD
TANK TRUCKS
SULFURIC ACID STORAGE
WATER AND WASHED UNREACTED BAUXITE
WASH TANK
CLEAR LIQUID
MUD
WASH TANK
FRESH WATER
WATER AND MUD TO POND
OVERFLOW WATER FROM POND

FIGURE 32
ALUMINUM SULFATE PROCESS AND TREATMENT FLOW DIAGRAM AT PLANT 049

The raw material bauxite contains 54-56 percent of soluble Al_2O_3, about 3.5 percent TiO_2, about 5.5 percent SiO_2, about 1.5 percent Fe_2O_3 and the rest water of hydration. The muds have, approximately, the following compositions: 40 percent SiO_2, 40 percent TiO_2, 20 percent Al_2O_3, 0.5 percent $Al_2(SO_4)_3$.

At these plants, all waters are fed to a settling basin where muds are removed and impounded. The clear effluent is then reused in the process. Provisions are established for collection of all leaks and spills which are pumped to the impoundment, treated and recycled. A breakdown of water use at both facilities is shown below:

Input Type	Plant	Quantity cu m/day	Quantity l/kkg	Comments
Well	049	47 (12,400 gpd)	1650 (396 gal/ton)	No Pretreatment Required for Either
Well	063	76 (20,000 gpd)	2090 (500 gal/ton)	

Process Water Type	Plant	Quantity cu m/day	Quantity l/kkg	Percent of Process Stream Recycled
Process	049	77 (20,400 gpd)	2720 (652 gal/ton)	30*
Process	063	87 (23,000 gpd)	2400 (575 gal/ton)	All excess process water*

---

*Remaining water shipped with product. Aluminum sulfate solutions are made at both plants.

These plants have no process or cooling water effluent.

Calcium Carbide

Calcium carbide is manufactured by the thermal reaction of calcium oxide and coke. Calcium oxide and dried coke are reacted in a furnace, and the product is then cooled, crushed, screened, packaged and shipped. The only wastes from the process are airborne dusts from the furnace, coke dryer and screening bag filters. Bag filters are now being installed in the furnace and the packing areas of plant 190. All collections are returned to the furnace. The process locations of the sources of raw waste in plant 190 are shown in Figure 33. A listing of the raw wastes and amounts is given below. All but the cooling tower blowdowns are treated by dry collection methods. The blowdown wastes are intermittent and are currently untreated. This data was furnished by the manufacturer.

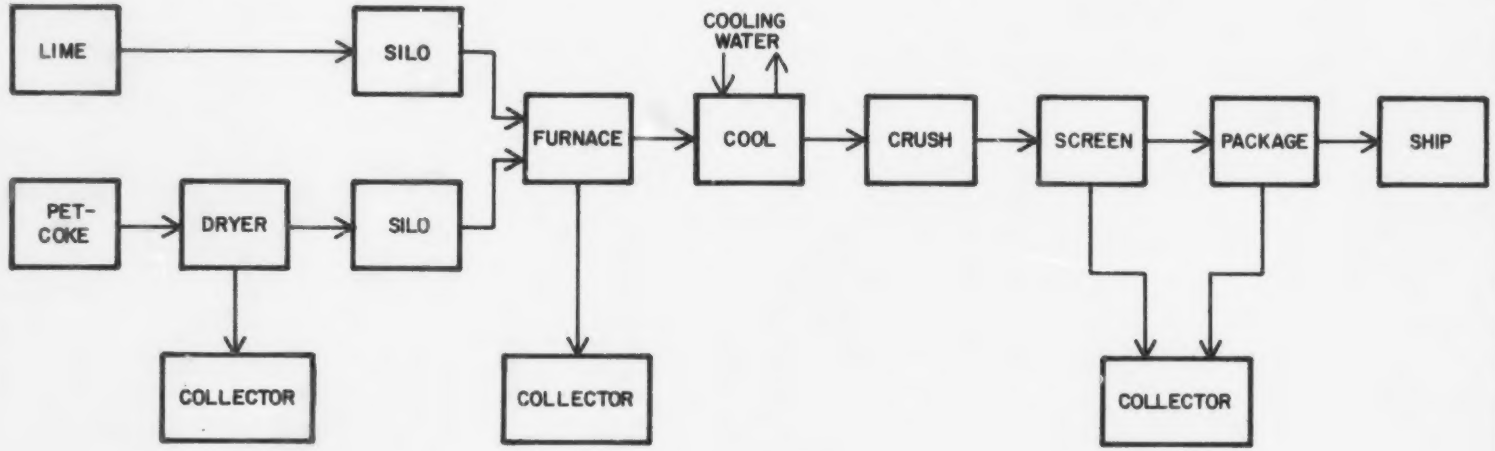
LIME
SILO
PET-COKE
DRYER
SILO
COLLECTOR
FURNACE
COLLECTOR
COOLING WATER
COOL
CRUSH
SCREEN
PACKAGE
SHIP
COLLECTOR

FIGURE 33
CALCIUM CARBIDE PROCESS FLOW DIAGRAM AT PLANT 190

Waste Product	kg/kkg of Product (lb/ton)	
	Average	Range
1. Fine Petroleum Coke	50 (100)	30-70 (30-140)
2. Stack Dust	85 (170)	70-115 (140-230)
3. Packing Dust	10 (20)	6-11 (12-22)
4. Cooling Tower Blowdown Solids and Cooling Water Treatment Chemicals		0.5-1 (1-2)

The first waste is collected by bag filters and recycled. Waste products 2 and 3 are now being exhausted to the air but will be collected and recycled by bag filters similar to those now collecting the coke fines. The fourth waste is currently untreated.

Figure 34 shows, schematically, the source and disposition of the water uses at this plant. Table 3 lists the effluent waste data supplied by plant 190 and verification measurements. (These data are the same as presented to the Corps of Engineers in plant 190's permit application, except for pH and flow, which were obtained during a plant visit).

Considerable amounts of chlorides and sulfates are discharged intermittently due to cooling tower blowdowns and use of water treatment chemicals.

Plant 190's policy is to recover and recycle all possible airborne dusts by dry collection techniques. This approach eliminates all process water wastes. The cooling tower blowdown and incoming water treatment regenerants are the only water effluents. There is no process waste water effluent in this exemplary plant.

Calcium Chloride

Calcium chloride is produced by extraction from natural brines. Some material is also recovered as a by-product of soda ash manufacture by the Solvay process. The latter will be discussed in the soda ash section.

In the manufacture of calcium chloride from brines, the salts are solution mined and the resulting brines are first partly evaporated to remove sodium chloride by precipitation. The brine is further purified by addition of other materials to remove sodium, potassium and magnesium salts by precipitation and further evaporation. It is then evaporated to dryness to recover calcium chloride which is packaged and sold. Figure 35 shows the detailed separation procedure used at plant 185. Bromides and iodides are first separated from the brines before sodium chloride recovery is performed. There is a large degree of brine

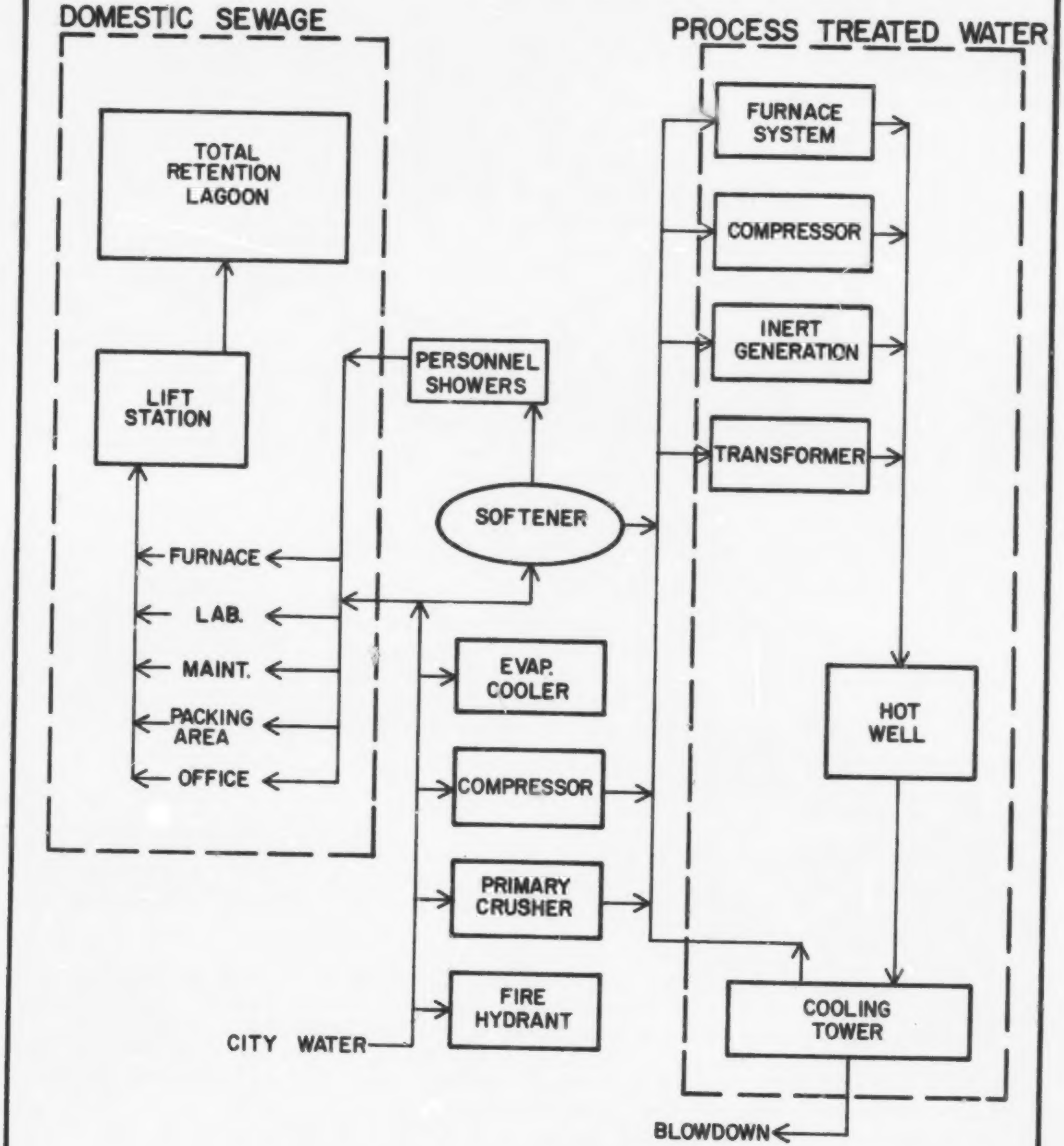
DOMESTIC SEWAGE
TOTAL RETENTION LAGOON
LIFT STATION
FURNACE
LAB.
MAINT.
PACKING AREA
OFFICE
PERSONNEL SHOWERS
SOFTENER
EVAP. COOLER
COMPRESSOR
PRIMARY CRUSHER
FIRE HYDRANT
CITY WATER
PROCESS TREATED WATER
FURNACE SYSTEM
COMPRESSOR
INERT GENERATION
TRANSFORMER
HOT WELL
COOLING TOWER
BLOWDOWN

FIGURE 34
WATER USAGE AT PLANT 190
CALCIUM CARBIDE FACILITY

TABLE 3. Plant Effluent from CaC_2 Manufacture
(All units ppm unless specified)

	Intake Water		Cooling Tower Water	
Parameter	Plant Data	Verifcn.	Plant Data	Verifcn.
Total suspended solids	3.5	0	48	0
Flow (cu m/day)	152	(a,b)	13	(a,b)
Total dissolved solids	238	(a)	1930	(a)
Conductivity (as NaCl)	(c)	95-100	(c)	810
BOD	80	(a)	308	(a)
COD	15	25	170	75
pH	7.6	7.5	7.6	8.0
Alkalinity (as $CaCO_3$)	99	90	68	165
Nitrate (as N)	0.45	0.27	12	9.8
Zinc	0.01	(a)	2.8	(a)
Phosphorus Total (phosphate)	0.27	0.32	0.55	1.30
Color (APHA Units)	Nil	10	675	20
Aluminum	0.15	(a)	0.17	(a)
Turbidity (FTU)	0	5	18	10
Fluoride	0.45	(a)	0.95	(a)
Total hardness (as $CaCO_3$)	140	136	404	750
Calcium hardness (as $CaCO_3$)	(c)	118	(c)	675
Sulfate	55	51.5	290	690
Chloride	46	36	198	95
Iron	0.03	0.08	-	0.019
Chlorine (as Cl_2)	(c)	0	(c)	0.1

(a) Not measured
(b) Flow varied frequently, depending on response of level-monitoring valve
(c) Not in furnished data.

Note: Above data are not from split samples, but represent data furnished for Corps of Engineer permit application approximately two years prior to the verification measurements.

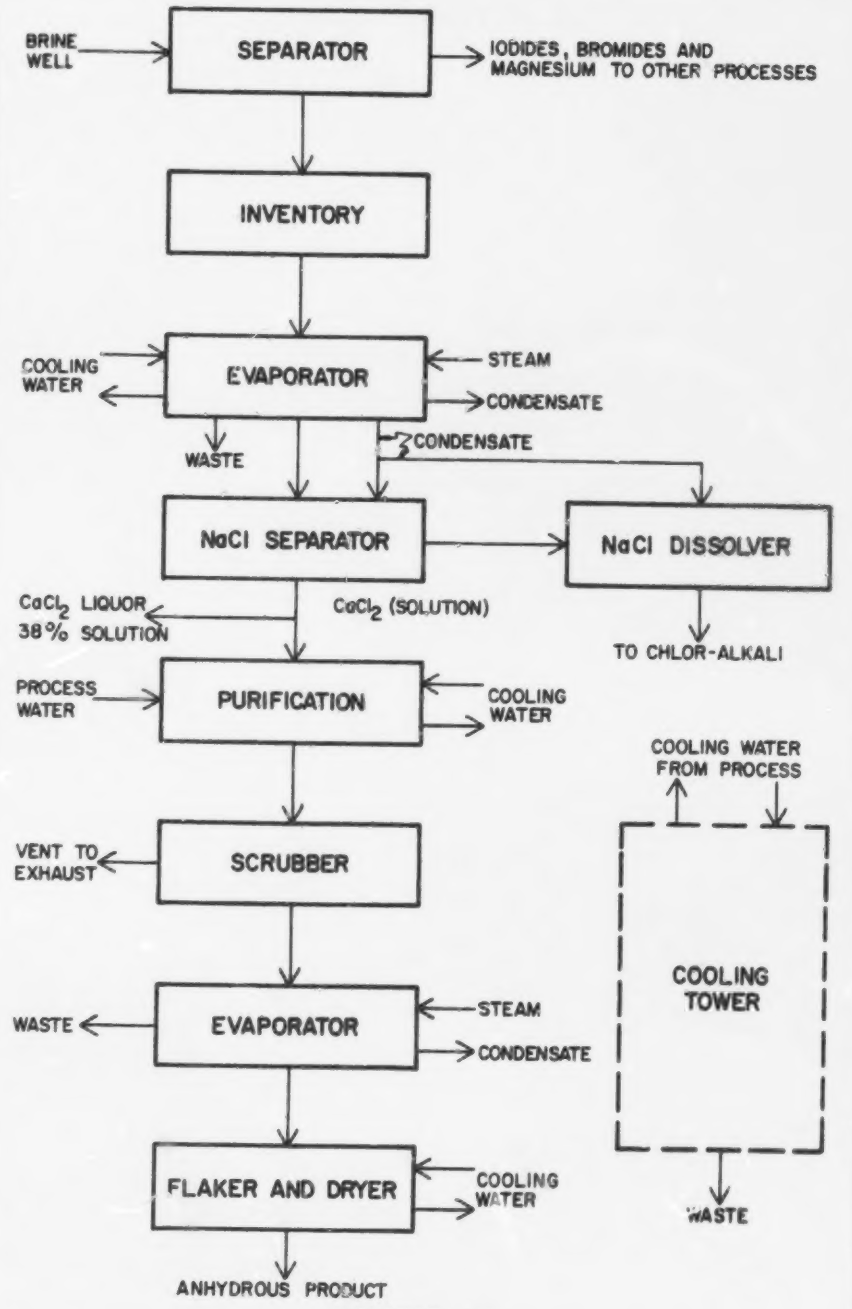
BRINE WELL
SEPARATOR
IODIDES, BROMIDES AND MAGNESIUM TO OTHER PROCESSES
INVENTORY
COOLING WATER
EVAPORATOR
STEAM
CONDENSATE
WASTE
CONDENSATE
NaCl SEPARATOR
NaCl DISSOLVER
$CaCl_2$ LIQUOR 38% SOLUTION
$CaCl_2$ (SOLUTION)
TO CHLOR-ALKALI
PROCESS WATER
PURIFICATION
COOLING WATER
COOLING WATER FROM PROCESS
VENT TO EXHAUST
SCRUBBER
COOLING TOWER
WASTE
EVAPORATOR
STEAM
CONDENSATE
FLAKER AND DRYER
COOLING WATER
WASTE
ANHYDROUS PRODUCT

FIGURE 35
CALCIUM CHLORIDE FLOW DIAGRAM AT PLANT 185

recycling to remove most sodium chloride values. The composition of the brine is:

$CaCl_2$	19.3 percent
$MgCl_2$	3.1 percent
NaCl	4.9 percent
KCl	1.4 percent
Bromides	0.25 percent
Other minerals	0.5 percent
Water	70.6 percent

The raw wastes expected from calcium chloride manufacture at plant 185 arise from blowdowns as well as from the several partial evaporation steps used. Most of the wastes are weak brine solutions:

Waste Products	Process Source	Avg. kg/kkg of Product (lb/ton)
NH_3	Evaporators	0.55 (1.1)
$CaCl_2$	Evaporators	29 (58)
NaCl	Evaporators	0.5 (1.0)
$CaCl_2$	Packaging	0.7 (1.4)
*NaCl & KCl	Brine Separation	45.5 (91)
*NaCl	Secondary Brine Separation	110 (220)

---

*Recycled or used elsewhere.

At plant 185, the waste brine streams are passed through an activated sludge treatment to remove organics and are then passed to a settling basin to remove suspended matter, adjusted to neutral pH, fed into a second pond to further settle suspended matter, and finally discharged. Future plans at plant 185 call for changes in the evaporators to reduce calcium chloride discharges and eliminate ammonia from the discharges. More recycling of spent brines is also planned. Table 4 gives a detailed breakdown of current water usage at plant 185.

Table 4A lists the river intake and effluent compositions at plant 185. The effluent consists mostly of weak brine solutions (neutral pH).

Calcium Oxide and Calcium Hydroxide

Calcium oxide is manufactured by thermal decomposition of limestone in a kiln. The limestone is first crushed, then added to the kiln, wherein it is calcined to effect decomposition. The product is then removed from the kilns, marketed as is, or slaked by reaction with water to produce calcium hydroxide. A process flowchart is given in Figure 36 descriptive of the general process at plant 007.

TABLE 4. Plant 185 Water Flows

A. Inputs

Type	cu m/day (MGD)	liters/kkg (gal/ton)
River (+ 44%)	31,100 (8.208)	62,700 (15,000)
Lake	545 (0.144)	1,100 (263)

B. Water Usage

Type	cu m/day (MGD)	liters/kkg (gal/ton)	% Recycled
Cooling	58,500 (15.5)	118,000 (28,300)	46
Process	164,000 (43.2)	330 (79)	0
Washdown	2,180 (0.576)	4,390 (1,052)	0
Washout	680 (0.180)	1,370 (329)	10

TABLE 4A Composition of Intake and Effluent Stream of Plant 185

	Intake		Effluent Stream No. 1	
Parameter*	Plant Data	Verification Measurement	Plant Data	Verification Measurement
Flow, cu m/day (MGD)	31,600 (8.35)	**	31,600 (8.35)	**
Total Suspended Solids	42	8	-	29
Total Dissolved Solids	353	293	2,693	309
BOD	3	-	1.1	-
COD	-	-	-	-
pH	8.3	8.3	6.7-8.0	9.1
Turbidity (FTU)	5.3	0	18.2	25
Color (ALPH Units)	20	70	60	80
Conductivity (NaCl)	476	520	5,390	340
Hardness (Ca)	200	179	700	169
Sulfate	110	36	312	36
Nitrate	0.2	0.29	0.2	20
Ammonia	0.1	0.60	2.0	8.8
Organic Nitrogen	0.2	-	2.7	-
Iron	0.4	0.30	1.0	0.09
Copper	-	-	-	-
Chromate	0.1	-	0.1	-
Manganese	0.05	-	0.1	-
Zinc	0.1	-	0.85	-
Total Alkalinity ($CaCO_3$)	160	170	67	235

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* mg/l unless otherwise specified

**measurement not possible due to physical constraints of location

Note: Above data not split samples; plant data furnished separately, prior to sampling for verification.

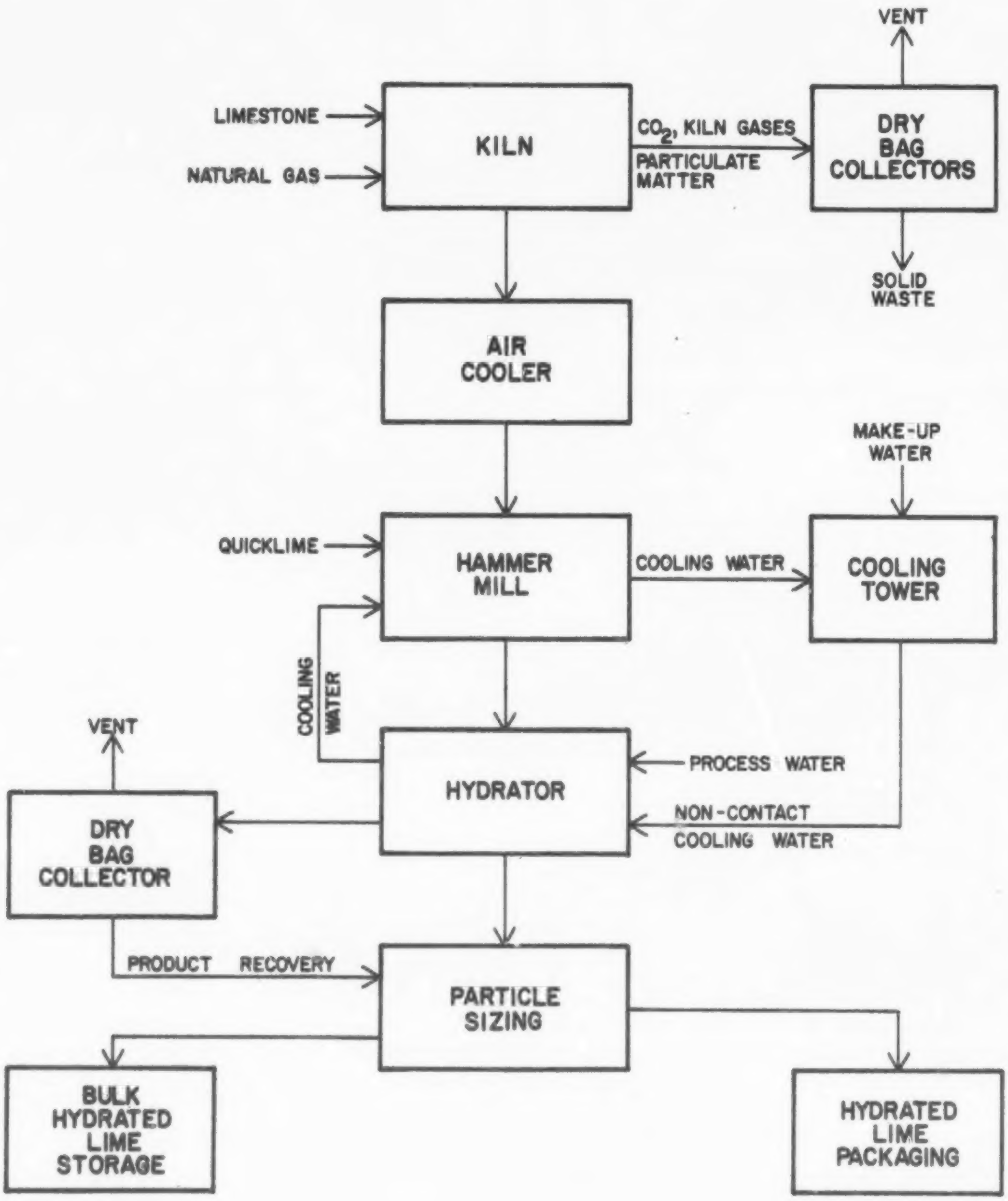
VENT
LIMESTONE
NATURAL GAS
KILN
CO2, KILN GASES
PARTICULATE MATTER
DRY BAG COLLECTORS
SOLID WASTE
AIR COOLER
MAKE-UP WATER
QUICKLIME
HAMMER MILL
COOLING WATER
COOLING TOWER
COOLING WATER
VENT
HYDRATOR
PROCESS WATER
NON-CONTACT COOLING WATER
DRY BAG COLLECTOR
PRODUCT RECOVERY
PARTICLE SIZING
BULK HYDRATED LIME STORAGE
HYDRATED LIME PACKAGING

FIGURE 36
FLOW DIAGRAM FOR LIME PLANT 007

The raw wastes produced from calcium oxide manufacture are shown below. The quantities of waste are not affected by process startup or shutdown. These consist of fine dusts collected from the plant gas effluent by scrubbing systems. At the exemplary facility, this dust removal is achieved by use of bag filters and other dry particulate collection equipment. No wet scrubbing techniques are employed. Wet scrubbing of these dusts is used commonly at other plants.

Waste Product	Process Source	kg/kkg of Product (lb/ton)
Dry Particulate Matter	Kiln gases (Dry collector)	67 (133)

Exemplary plant water usage is described below. All cooling water is recycled and all product water is consumed in the manufacture of calcium hydroxide. Due to the use of dry waste collection techniques, there is no waterborne effluent from the facility. This plant achieves ninety-five percent or better solids collection at the kiln collector. Municipal water intake to the plant amounts to 638 l/kkg (153 gal/ton) of product plus the amount evaporated in the cooling tower. This water is not further treated in the plant prior to use.

This water represents the process water, which is used in the hydrator. The cooling water flow for the bearings on the tube mill and pistons on the hydrator pump amounts to 1000 l/kkg of product (240 gal/ton). It is completely recycled with makeup water added to compensate for evaporation.

Chlorine and Sodium or Potassium Hydroxide

a) Mercury cell process

Caustic and chlorine are produced from sodium chloride or potassium chloride raw materials in the mercury cell process, depending on whether caustic soda or caustic potash is to be produced. The raw material is dissolved and purified by addition of barium carbonate, soda ash, and lime to remove magnesium and calcium salts and sulfates prior to electrolysis. The insolubles formed on addition of the treatment chemicals are filtered from the brine. The brine is then fed to the mercury cell, wherein chlorine is liberated at one electrode and a sodium-mercury amalgam is formed at the other.

The chlorine formed is cooled, dried in a sulfuric acid stream, purified to remove chlorinated organics, compressed and sold. The mercury-sodium amalgam also formed during electrolysis is sent to a "denuder" where it is treated with water to decompose the amalgam. Sodium hydroxide and hydrogen are formed in the reaction. The mercury liberated is returned to the electrolysis cells. The hydrogen is cooled, scrubbed to remove traces of mercury, compressed and sold.

The sodium hydroxide formed at the denuders is filtered, concentrated, and sold. Brines emerging from the electrolysis cells are concentrated and recycled.

Two exemplary facilities, plants 130 and 144, and one qualified exemplary facility, plant 098, have been selected and studied in detail. Plant 130 produces potassium hydroxide and plants 144 and 098 produce sodium hydroxide. Plant 098 is considered as an exemplary plant with the qualification that it is located outside of the United States. It is included because its mercury recovery system is of special note. The process flow diagram for plant 130 is shown in Figure 37.

Raw waste loads for this process are presented in Table 5, which gives overall figures based on twenty-one facilities, plus partial data as furnished from plants 098 and 130. The chief raw wastes include purification muds ($CaCO_3$, $Mg(OH)_2$ and $BaSO_4$) from brine purification, some spent brine materials from caustic recovery, and condensates from chlorine and hydrogen compressions. The sulfuric acid used to dry the chlorine is not a waste in plant 130 as it is recovered for sale.

In the caustic potash plant, plant 130, the brine muds and potassium chloride make up the bulk of the primary waste. A small amount of copper sulfate catalyst is also wasted. This catalyst is used in treatment of waste chlorine. Specifically, the chlorine is reacted with excess sodium hydroxide in the presence of copper sulfate to produce sodium chloride, water and oxygen. The sodium chloride so produced is sent to the waste treatment facilities.

At plant 144, the wastes emerging from chlor-alkali manufacture are sent to a series of two settling ponds, with the exception of those from the cell building, which are sent to a mercury treatment unit first. The wastes from chlorine drying, brine preparation, salt saturation and caustic loading are sent directly to the two settling ponds described above, where suspended solids are removed and the pH adjusted prior to discharge. Two emergency ponds are in parallel with these two ponds and wastes can be diverted to them for special treatment if needed.

Mercury-containing wastes from the cell building are first treated prior to being sent to the central waste treatment system. The effectiveness of treatment based on six months of data (129 days of measurements) is, in summary:

	Mercury Concentration to Secondary Treatment (mg/l)	Mercury Concentration after Treatment (mg/l)	Average Removal Efficiency (percent)
Average	44.3	0.43	99.0
Maximum values	1920.0	15.0	-
Minimum values	0.48	0.01	-

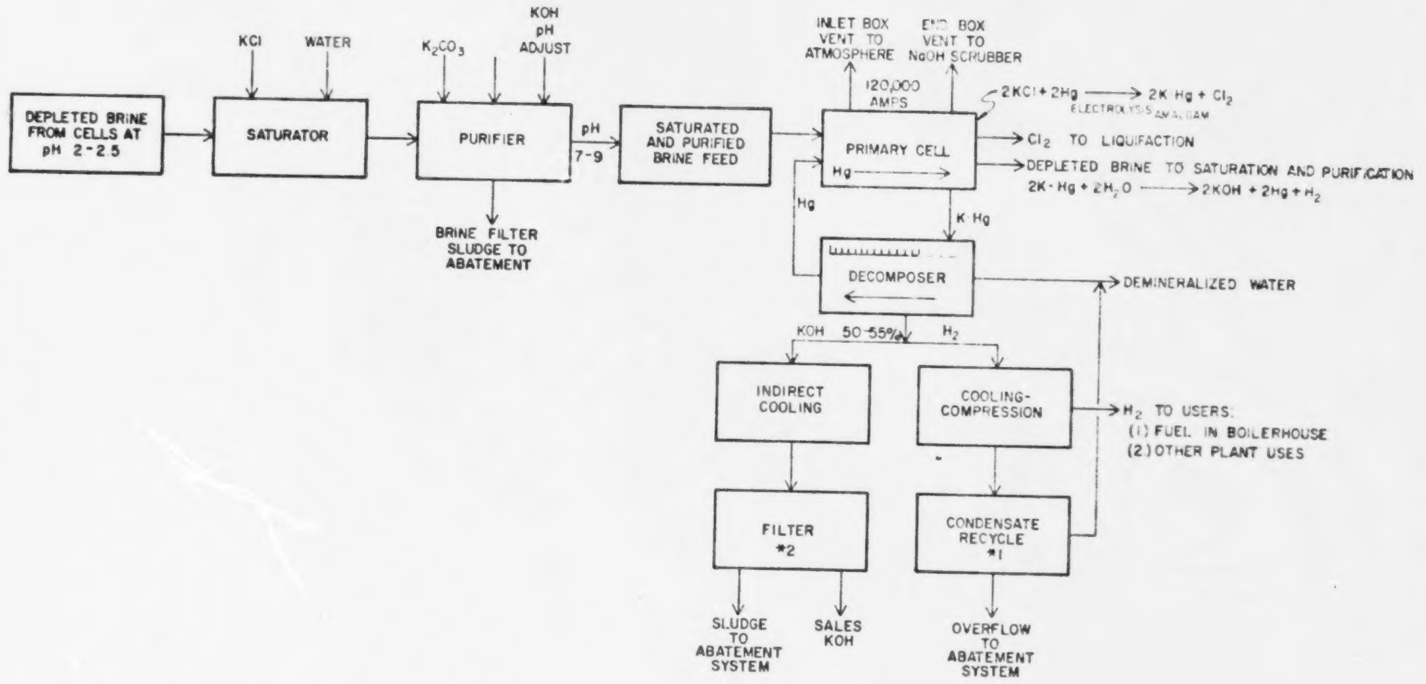
DEPLETED BRINE FROM CELLS AT pH 2-2.5
KCl
WATER
SATURATOR
K_2CO_3
KOH pH ADJUST
PURIFIER
BRINE FILTER SLUDGE TO ABATEMENT
pH 7-9
SATURATED AND PURIFIED BRINE FEED
INLET BOX VENT TO ATMOSPHERE
END BOX VENT TO NaOH SCRUBBER
120,000 AMPS
$2KCl + 2Hg \xrightarrow[\text{ELECTROLYSIS}]{} 2K{\cdot}Hg + Cl_2$
AMALGAM
PRIMARY CELL
Hg
Cl_2 TO LIQUIFACTION
DEPLETED BRINE TO SATURATION AND PURIFICATION
$2K{\cdot}Hg + 2H_2O \longrightarrow 2KOH + 2Hg + H_2$
Hg
K·Hg
DECOMPOSER
DEMINERALIZED WATER
KOH 50-55%
H_2
INDIRECT COOLING
COOLING-COMPRESSION
H_2 TO USERS:
(1) FUEL IN BOILERHOUSE
(2) OTHER PLANT USES
FILTER *2
CONDENSATE RECYCLE *1
SLUDGE TO ABATEMENT SYSTEM
SALES KOH
OVERFLOW TO ABATEMENT SYSTEM

FIGURE 37
MERCURY CELL FLOW DIAGRAM (KOH) AT PLANT 130

TABLE 5. Raw Waste Loads from Mercury Cell Process (All Amounts in kg/kkg of Chlorine)*

	Based on 21 Facilities		Plant 098	Plant 130	
	Mean	Range		Mean	Range
Purification muds, $CaCO_3$ & $Mg(OH)_2$	16.5	0.5-35	7.25	7.5	6.8-7.9
NaOH	13.5	0.5-32	-	-	-
NaCl	211	15-500	-	40	35-45
KCl	0	-	0	50	45-54
H_2SO_4	16	0-50	11.3	0	-
Chlorinated Hydro-carbons**	0.7	0-1.5	-	-	-
Na_2SO_4	15.5	0-63	-	-	-
Cl_2 (as $CaOCl_2$)	11	0-75	-	-	-
Filter aids	0.85	0-5	1.83	-	-
Mercury	0.15	0.02-0.28	0.0018	-	-
Carbon, graphite	20.3	0.35-340	-	-	-
$CuSO_4$	0	-	0	0.004	-

---

*can be converted to lb/ton of product by multiplication by 2.0.
**depends markedly on grade of chlorine produced.

Approximately 99 percent removal of mercury is achieved with the mercury losses from the facility being kept to about 0.0045-0.0237 kg/day (0.01-0.05 lb/day) for the most part. Figure 38 gives a histogram of the mercury discharges on a daily total quantity basis. The mean value of this discharge parameter is 0.0178 kg/day (0.03882 lb/day) or 0.000070 kg/kkg of chlorine (0.000140 lb/ton of chlorine). Ninety-one percent of the measurements fell below 0.00014 kg/kkg.

At plant 098, several of the streams are completely recycled to minimize brine wastes. Treatment of mercury-containing streams makes use of sodium sulfide to precipitate mercury and mercury sulfides. These materials are filtered from the streams, recovered as solids and treated with sodium hypochlorite to recover mercury (as chloride). The leached solids can then be safely discarded and the mercury chloride-containing solutions can be used for brine makeup and returned to the cells where the mercury chloride is decomposed to elemental mercury for reuse.

The mercury effluent and chlorine treatment effectiveness at plant 098 are as follows:

Method	Qualitative Rating*	Waste Reduction Accomplished
Mercury Recovery Unit	Excellent	97 percent recovery of mercury
Chlorine Neutralization System	Excellent	100 percent removal of chlorine from waste gas stream
Hydrogen Peroxide Treatment of liquid effluent	Good	100 percent removal of available chlorine

*As rated by plant personnel.

The mercury discharged and recovered from the sulfide treatment system over a two month period in 1972 from this plant averaged 0.0108 kg/day (0.0237 lb/day) or 0.000069 kg/kkg (0.000138 lb/ton) of chlorine. Analysis of the data for the two month period showed that the average mercury recovery was 258 kg/day (568 lb/day) or 7.5 kg/kkg (15.0 lb/ton) of chlorine. At the plant 130 mercury cell facility, brine filter sludges, potassium hydroxide recovery wastes and other waste streams are fed into a common treatment system, wherein the wastes are treated with sodium hydrosulfide and flocculants. The insoluble mercury products from treatment are removed by settling and filtration and the wastes are then discharged. The mercury content of the

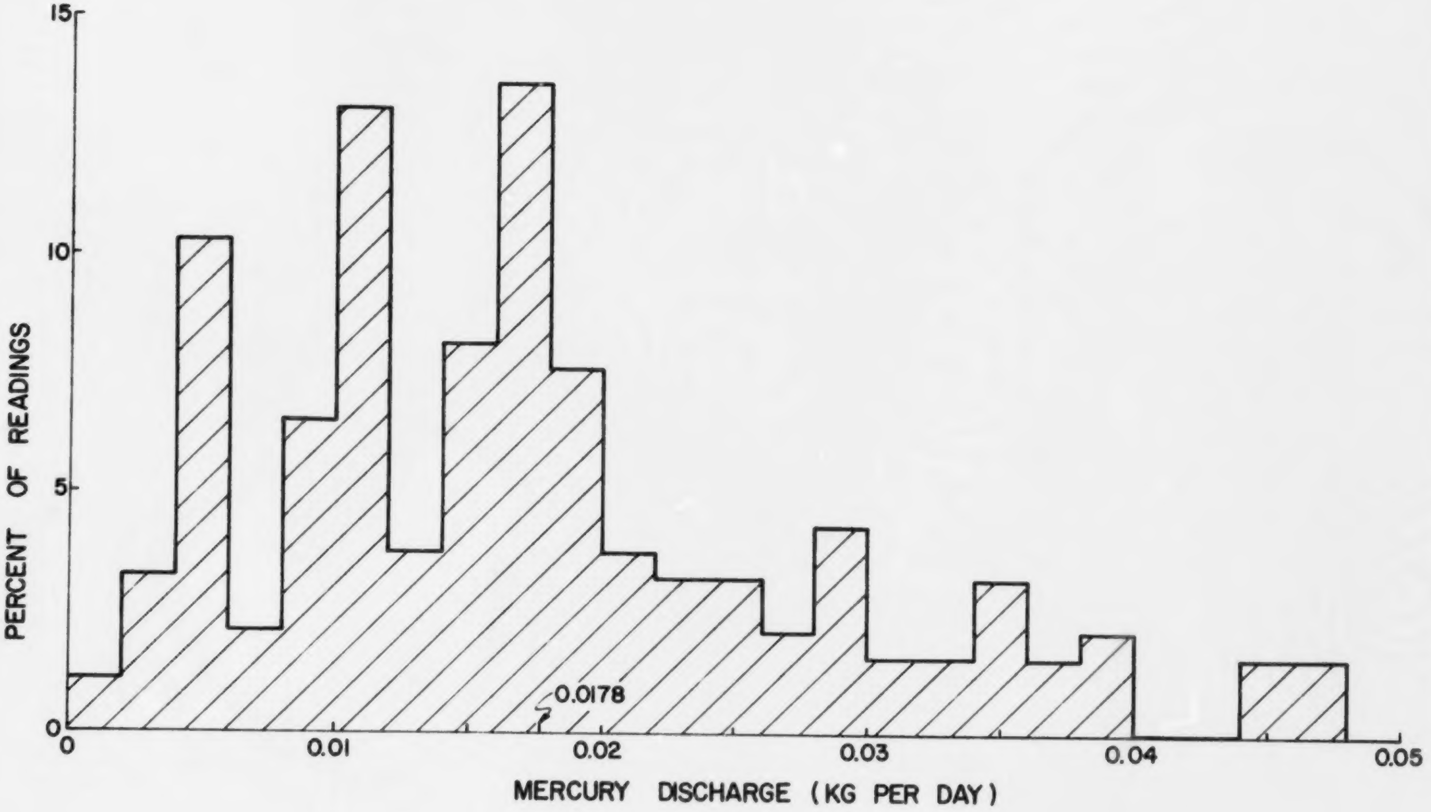

FIGURE 38
HISTOGRAM OF MERCURY DISCHARGES FROM PLANT 144

wastes is recovered by distillation from the recovered sludges. The mercury treatment system is shown in Figure 39.

Table 6 summarizes the mercury effluents from plant 130 as a result of treatment over a one-year period. The mean mercury effluent level of 0.0073 kg/day (0.016 lb/day) corresponds to a value of 0.000057 kg/kkg (0.000114 lb/ton) of chlorine, similar to the 0.000069 kg/kkg (0.000138 lb/ton) calculated for the 098 plant and the 0.000070 kg/kkg (0.000140 lb/ton) for the 144 mercury cell plant.

The general characteristics of the 098 plant discharge are listed below. The seawater cooling water stream is mixed with the process water effluent prior to discharge, hence the high TDS:

	Average	Range
Total Suspended Solids, mg/l	5	5-10
Total Dissolved Solids, mg/l	-	20,000-25,000 (seawater)
pH	7.1	6.7-8.5
Temperature, °C (°F)	12 (54)	10-19 (50-66)
Hydrogen Peroxide, mg/l	0	0-1.0
Sodium Sulfide, mg/l	0	0-0.5
Free Chlorine, mg/l		Max. 0.08
Mercury, mmg/l		Max. 8.0

Tables 7 and 8 give the plant 130 effluent stream data and verification data. Tables 9 and 10 give the plant 144 intake and effluent streams data with verification data.

b) Diaphragm cell process

The plant 057 facility described in this section is part of an integrated complex using a considerable amount of recycling and reuse technology.

Sodium chloride brines are first purified by addition of sodium carbonate, flocculating agents and sodium hydroxide in the amounts required to precipitate all the magnesium and calcium contents of the brine. The brine is then filtered to remove the precipitated materials and electrolyzed in a diaphragm cell. Chlorine, formed at one electrode, is collected, cooled, dried with sulfuric acid, then purified, compressed, liquified and shipped. At the other electrode, sodium hydroxide is formed and hydrogen is liberated. The hydrogen is cooled, purified, compressed and sold. The sodium hydroxide formed, along with unreacted brine, is evaporated to 50 percent concentration. During the partial evaporation, most of the unreacted sodium chloride precipitates from the solution, which is then filtered. The collected sodium chloride is recycled to the process, and the sodium hydroxide solutions are further evaporated to yield solid products.

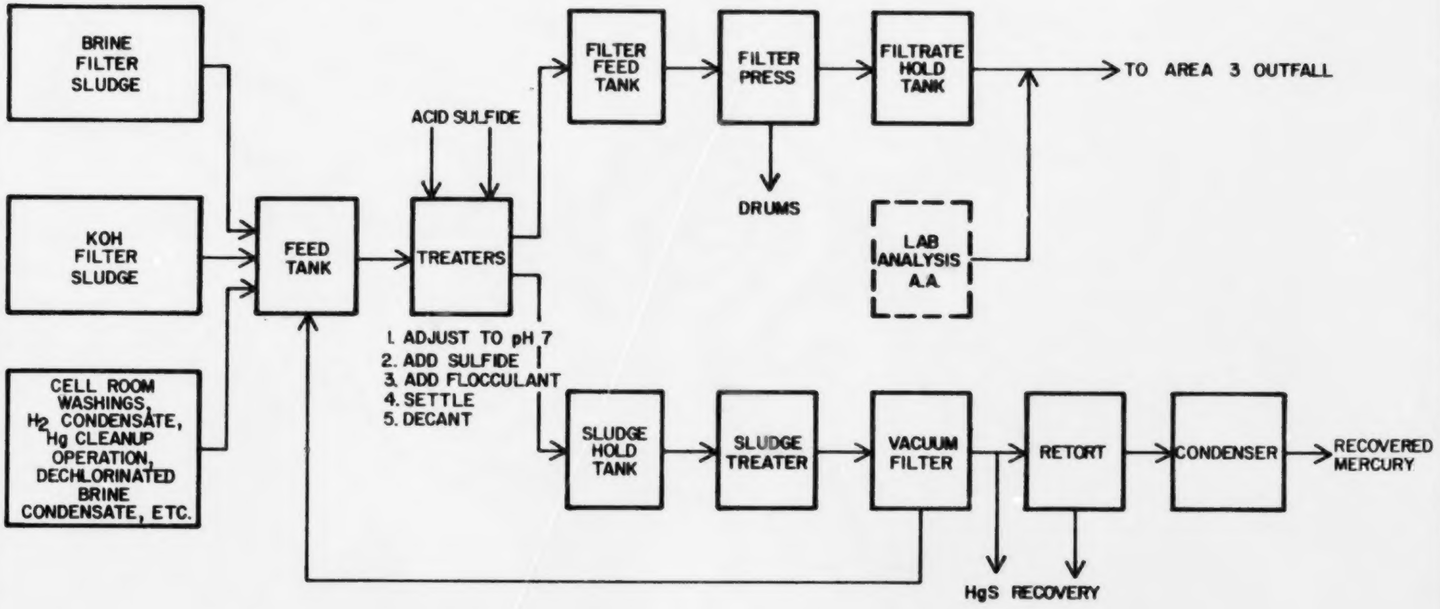
BRINE FILTER SLUDGE
KOH FILTER SLUDGE
CELL ROOM WASHINGS, H_2 CONDENSATE, Hg CLEANUP OPERATION, DECHLORINATED BRINE CONDENSATE, ETC.
FEED TANK
ACID SULFIDE
TREATERS
1. ADJUST TO pH 7
2. ADD SULFIDE
3. ADD FLOCCULANT
4. SETTLE
5. DECANT
FILTER FEED TANK
FILTER PRESS
DRUMS
FILTRATE HOLD TANK
LAB ANALYSIS A.A.
TO AREA 3 OUTFALL
SLUDGE HOLD TANK
SLUDGE TREATER
VACUUM FILTER
RETORT
CONDENSER
RECOVERED MERCURY
HgS RECOVERY

FIGURE 39
MERCURY ABATEMENT SYSTEM AT PLANT 130

TABLE 6. Monthly Mercury Abatement System Discharge During 1972 at Plant 130

Month	Average Volume Discharge cu m(gal)/day	Total Hg Discharge kg (lb)	Average Daily Hg Discharge kg(lb)/day	Average mcg/l Hg
Jan	144 (37,916)	0.369 (0.813)	0.012 (0.026)	82
Feb	118 (31,030)	0.327 (0.719)	0.011 (0.024)	92
Mar	92 (24,195)	0.198 (0.435)	0.0064 (0.014)	69
Apr	112 (29,616)	0.184 (0.404)	0.0059 (0.013)	53
May	115 (30,339)	0.318 (0.700)	0.010 (0.023)	91
Jun	134 (35,277)	0.214 (0.471)	0.0068 (0.015)	51
Jul	124 (32,709)	0.225 (0.494)	0.0073 (0.016)	59
Aug	137 (36,169)	0.302 (0.665)	0.0096 (0.021)	72
Sep	131 (34,435)	0.127 (0.280)	0.0041 (0.009)	31
Oct	129 (34,024)	0.133 (0.293)	0.0041 (0.009)	33
Nov	126 (33,339)	0.176 (0.377)	0.0055 (0.012)	43
Dec	118 (31,135)	0.144 (0.251)	0.0036 (0.008)	31
Av.	123 (32,516)	0.224 (0.492)	0.0073 (0.016)	59

Statistical Summary: Mercury Abatement System Jan-Aug 1972 - Total of 244 Days

	Daily Mercury Discharge, kg (lb)/day	Daily Volume Discharge, cu m (gal)/day
Mean	0.0086 (0.019)	122 (32,164)
Range, Max.	0.0545 (0.120)	292 (63,945)
Standard Deviation	0.0077 (0.017)	40 (10,492)
90% of Values	0.0182 (0.040)	173 (45,594)

TABLE 7. Plant 130 Effluent Data*

	Outfall #1	Outfall #2	Outfall #3**	Intake
Flow, cu m/day (MGD)	9,460(2.5)	13,300(3.5)	42,400(11.2)	-
Total Suspended Solids	5	-	-	-
pH	8-11	8-9	8-9	-
Color (APHA Units)	-	-	-	5
Conductivity, umhos	-	-	-	287
Hardness, (Total) ($CaCO_3$)	-	-	400	134
Chloride	-	-	1252	22
Free Chlorine	-	-	0	0
Fluoride	-	-	1	1
Phosphates (as P)	-	-	-	0.1
Nitrate (as N)	-	-	1.92	1.92
Iron	-	-	1.2	1.0
Copper	-	-	-	0.01
Chromium	-	-	0.01	0.01
Manganese	-	-	-	
Vanadium	-	-	-	-
Arsenic	-	-	-	0.28
Mercury, mcg/l	-	-	1.2	1
Lead	-	-	0.1	0.1
Sulfate	-	-	39	18
Turbidity	-	-	-	16

---

*Data supplied by Plant 130, mg/l unless otherwise specified.

**Main outfall, outfalls 1 & 2 feed into 3. This waste stream contains potassium carbonate manufacturing effluent also.

TABLE 8. Measurements of the Effluents From Plant 130

Parameter*	River (Intake)	Hg Cell Chlorine Liquefaction**	Abatement**	Major Outfall**
Flow, cu m/day (MGD)	Not Measured	8,540(2.25)	16,700(4.28)	42,000(11.1)
Temp., °C	2.0	11.95	10.1	8.5
Color, Apparent, APHA Units	60	60	180	150
Turbidity, FTU	23	19	55	50
Conductivity, mhos/cm	230	240	320	370
Suspended Solids,	70	210	75	210
pH	7.8	11.9	9.4	10.5
Alkalinity (Total)				
P ($CaCO_3$)	0	40	30	25
T ($CaCO_3$)	97	180	135	200
Hardness, (Total) ($CaCO_3$) mg/l	145	60	140	65
Calcium ($CaCO_3$)	115	25	110	35
Chlorine	0	0.2	0.3	0
Chloride	35	47.5	60	48.5
Fluoride	0	0	0	0
Sulfate	45	44	41	40
Phosphates (Total)	0.38	0.4	0.42	0.37
Nitrogen (Total)	1.55	0.45	0.13	0.38
Iron	0.19	0.5	0.7	0.4
Dissolved oxygen	***	8.3	7.6	8.5
Mercury, mcg/l	5	5	5	5

---

*mg/l unless otherwise specified.

**Corresponds to outfalls #1, 2 and 3 respectively on Table 21.

***Unable to determine at temperature below 5°C.

TABLE 9. Plant 144 Intake Water

Parameter*		Plant Data**	GTC Measurement
Temperature, °C		8-24	19
Color, Apparent, APHA Units		-	175
Turbidity, FTU		-	50
Conductivity, mhos/cm		75	55
Suspended Solids		10	10
Dissolved Solids		65	-
pH		6.6	6.7
Acidity: Total		-	0 $CaCO_3$
Free		-	0 "
Alkalinity (Total)	P	-	0 "
	T	18	16 "
Hardness: Total		-	15 "
Calcium		-	5 "
Halogens: Chlorine		-	0.18
Chloride		-	15
Fluoride		-	0.1
Sulfate		-	8
Phosphates (Total)		-	0.34
Heavy Metals: Iron		-	0.48
Chromate (Cr^{+6})		-	0.02
Oxygen (Dissolved)		-	12
COD		15	10

---

*mg/l unless otherwise specified.

**Data from Corps of Engineers permit application, approximately two years prior to verification sampling.

TABLE 10. Plant 144 Effluent Data

Parameter*		Plant Data**	Verification Measurement
Flow, cu m/day (MGD)		5,300 (1.9)	8,360 (3.0)
Temperature, °C		32-38	33
Color, Apparent, APHA Units		-	30
Turbidity, FTU		-	10
Conductivity, mhos/cm		1,525	2,000
Suspended Solids		0	0
Dissolved Solids		1,455	1,777
pH		7.0	7.5
Acidity: Total		-	0 $CaCO_3$
Free		-	0 "
Alkalinity (Total)	P	-	0 "
	T	60	14 "
Hardness: Total		-	20 "
Calcium		-	10 "
Halogens: Chlorine		-	0
Chloride		-	1020
Fluoride		-	0.5
Sulfate		-	107
Phosphates (Total)		-	0.18
Heavy Metals: Iron		-	0.42
Chromate (Cr+6)		-	0.02
Oxygen (Dissolved)		-	10
COD		8	5
Mercury, mcg/l		3	5

---

*mg/l unless otherwise specified.

**Data from Corps of Engineers permit application, approximately two years prior to verification sampling.

Figure 40 shows the flow diagram of a 1810 kkg/day (2000 ton/day) chlorine-caustic soda plant. A new 2080 kkg/day (2300 ton/day) chlorine-caustic soda plant also exists in this facility. The sodium hydroxide product from these two plants is concentrated in another portion of plant 057. This function is illustrated in Figure 41. All three of these facilities (all parts of plant 057) will be discussed below.

There are no brine wastes from plant 057 and several of the other waste streams are diverted for other uses in the complex. This stream diversion and maximal raw material utilization has served to minimize the wastes to be treated. The raw wastes from the newer plant are:

Waste Product	Process Source	Ave. kg/kkg (lb/ton) of Cl_2
1. NaOCl	Gas Scrubber	1.13 (2.26) (Startup and shutdown)
2. $NaHCO_3$	Gas Scrubber	2.49 (4.58) (Wastes are ponded for recycle)
3. Chlorinated Organics	Liquefaction	0.35 (0.70)
4. Brine Sludge	Brine Treatment	10.5 (21)
5. Spent Sulfuric Acid	Chlorine Drying	1.0 (2.0)
6. Chromates	Cooling Tower	0.000363 (0.000726)
7. Suspended Solids	Cooling Tower	0.0333 (0.0666)

The raw wastes from the old plant are:

Waste Product	Process Source	Average kg/kkg of Chlorine (lb/ton)
1. Weak Caustic	Cells	66.25 (12.5)
2. Spent Sulfuric Acid	Chlorine Drying	4.05 (8.1)
3. NaOCl	Tail Gas Scrubber	7.50 (15.0)
4. Carbonate Sludge ($CaCO_3$)	Brine Treating	12.25 (24.5)
5. Chlorinated Hydrocarbons	Chlorine Purification	0.70 (1.4)

The raw wastes from the caustic plant are:

Waste Products	Process Source	Average kg/kkg of Product (lb/ton)
1. NaOH	Entrainment	4.4 (8.8)
2. NaCl	Entrainment	5.1 (10.2)
3. NaOH	Filter Wash	17.6 (35.2)
4. NaCl	Filter Wash	20.3 (40.6)

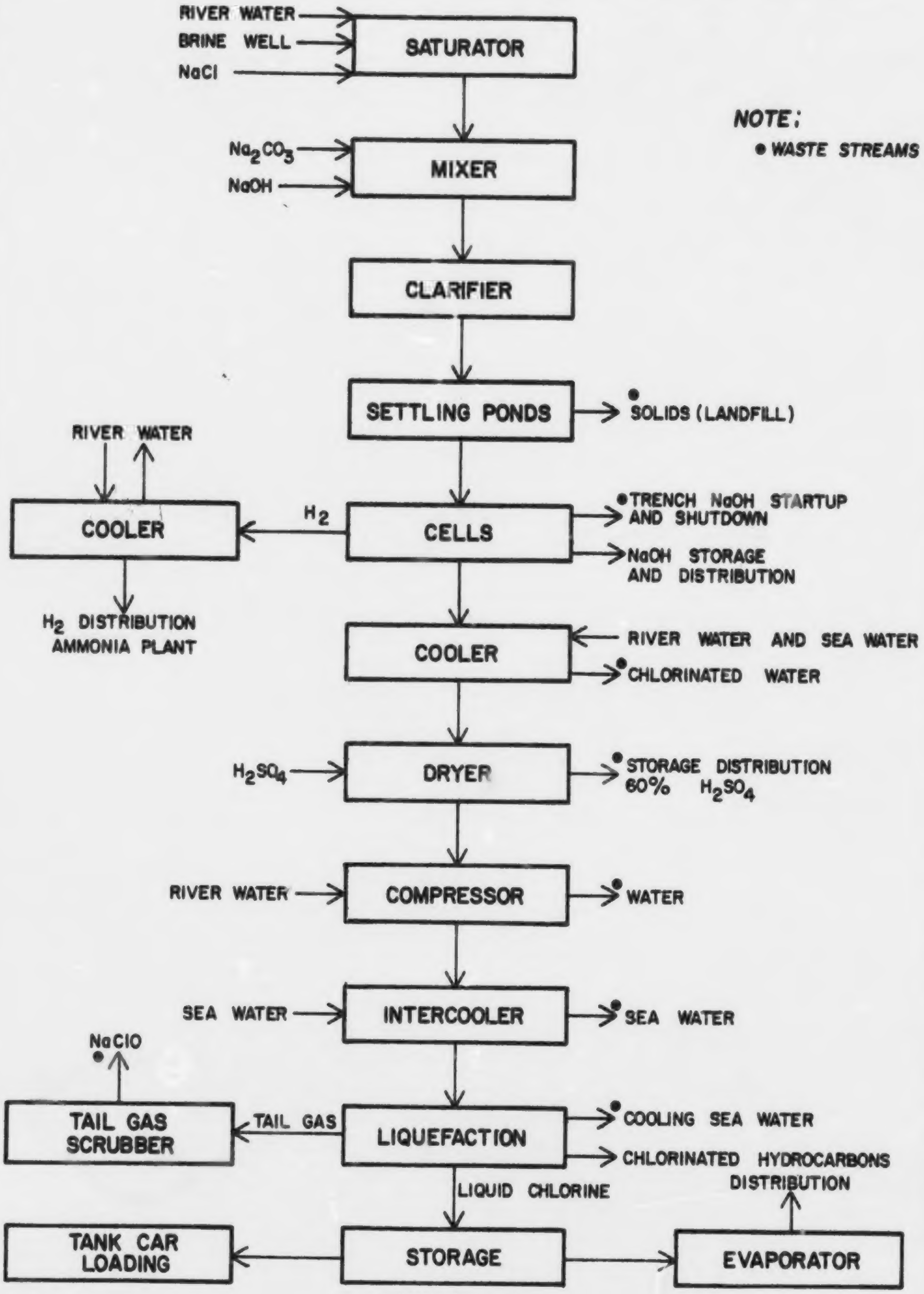
RIVER WATER
BRINE WELL
NaCl
SATURATOR
NOTE:
● WASTE STREAMS
Na_2CO_3
NaOH
MIXER
CLARIFIER
SETTLING PONDS
● SOLIDS (LANDFILL)
RIVER WATER
COOLER
H_2
CELLS
● TRENCH NaOH STARTUP AND SHUTDOWN
NaOH STORAGE AND DISTRIBUTION
H_2 DISTRIBUTION AMMONIA PLANT
COOLER
RIVER WATER AND SEA WATER
● CHLORINATED WATER
H_2SO_4
DRYER
● STORAGE DISTRIBUTION 60% H_2SO_4
RIVER WATER
COMPRESSOR
● WATER
SEA WATER
INTERCOOLER
● SEA WATER
● NaClO
TAIL GAS SCRUBBER
TAIL GAS
LIQUEFACTION
● COOLING SEA WATER
CHLORINATED HYDROCARBONS
DISTRIBUTION
LIQUID CHLORINE
TANK CAR LOADING
STORAGE
EVAPORATOR

FIGURE 40
DIAPHRAGM CELL CHLOR-ALKALI PROCESS
AT PLANT 057

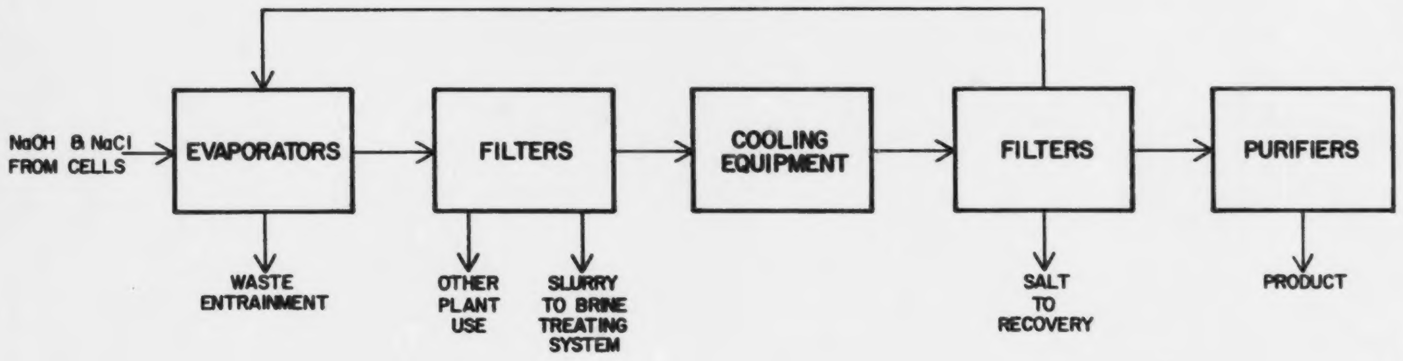
NaOH & NaCl FROM CELLS
EVAPORATORS
WASTE ENTRAINMENT
FILTERS
OTHER PLANT USE
SLURRY TO BRINE TREATING SYSTEM
COOLING EQUIPMENT
FILTERS
SALT TO RECOVERY
PURIFIERS
PRODUCT

FIGURE 41
SODIUM HYDROXIDE CONCENTRATION FACILITY AT PLANT 057

Many of the chlor-alkali waste streams, including brine wastes, are either recycled or put to use elsewhere in the complex. This section discusses treatment of those streams which are discharged.

The newer chlor-alkali plant takes in 2,720 cu m/day (0.72 mgd) of river water for cooling makeup and process water, as well as 54 cu m/day (0.0144 mgd) of well water for potable use. About 98.5 percent of the total cooling water flow of 109,000 cu m/day (28.8 mgd) is recycled, and 90 percent of the process water flow of 6040 cu m/day (1.6 mgd) is recycled. Of the potable water intake, 10 percent is recycled.

The waste treatment within this newer plant is:

Stream No./Source	Flow, l/day (gpd)	Treatment Method	Final Disposal
1/Gas Scrubber	409,000 (108,000)	Sunlight decomposition of NaOCl	To plant waste water system
2/Spent Sulfuric Acid	2,890 (765)	Other plant use	Used
3/Chlorine liquefaction	492 (130)	Incineration	---
4/Brine Treating	327,000 (86,400)	Solids to landfill	Brine recycled
5/Cooling Tower Blowdown	75,700 (20,000)	None	To plant waste water system

Waste chlorine in the tail gas is reduced by 80 percent in an absorption process, and the remaining chlorine is removed by scrubbing. These two processes are used in series to attain complete removal of chlorine from the tail gas.

Future treatment plans are:

Method	Estimated Installation Time	Estimated Performance
1. Chlorinated hydrocarbon waste burner	2 years	100 percent
2. Catalytic conversion of scrubber effluent to remove sodium hypochlorite	1 year	100 percent
3. Neutralization of scrubber effluent to remove sodium carbonate	1 year	100 percent

At the older chlor-alkali facility in plant 057, river water intake is 10,450 cu m/day (2.76 mgd) and seawater intake is 57,200 cu m/day (15.14 mgd). The cooling water flow is 61,000 cu m/day (16.13 mgd), which is all non-contact except for the water chlorination step. Process water flow is 6.530 cu m/day (1.726 mgd), which is mainly as brine. Other process water uses are compression cooling, hydrogen cooling, chlorine cooling and absorption. There is less recycling of water here than in the newer plant. The effluent stream which is not recycled arises from the tail gas scrubber, which has a flow of 133,000 l/day (35,000 gal/day) or 141 l/kkg (37.2 gal/ton) based on chlorine product. This is disposed of completely in the plant waste system. It contains sodium hypochlorite. The disposal of this material will be eliminated and the tail gas will be used to manufacture hydrochloric acid product, thus eliminating a waste stream. When this happens, the older process should be close to a nondischarge system.

The water intake to the caustic plant is:

	cu m/day (mgd)
river water	1,890 (0.50)
seawater	90,900 (24.0)
well water	57 (0.015)

The river water is treated; the well water is not. The in-plant water flows are:

	cu m/day (mgd)	% Recycled
Forced Draft Cooling	6,540 (1.73)	95
Process	1,300 (0.344)	0
Washdowns	265 (0.070)	0
Entrainment Seawater	90,900 (24.0)	0

The only effluent to be treated is 4.4 kg/kkg (8.8 lb/ton) of sodium hydroxide and 5.1 kg/kkg (10.2 lb/ton) of sodium chloride in a 90,900 cu m/day seawater waste stream (the entrained system). This system is presently discharged without treatment. Future plans call for it to be neutralized prior to discharge. Chloride values entrained in this stream are considered to be too low to be worthwhile for other plant usage. These three facilities are being improved to further reduce discharges.

The effluents from the newer chlor-alkali facility, the older facility and the sodium hydroxide plant are shown below.

Newer Plant:

Parameter	Average Concentration, mg/l Stream No. 1	2	3	4	5
Total Dissolved Solids	18,330 (mostly chlorides)	-	-	1200	820
Total Suspended Solids	14	-	-	22,500	256
BOD	0	0	0	0	0
COD	0	0	0	0	0
pH	7.8	1	-	11.0	7.0
Temperature, °C	38	Ambient	31	Ambient	32
Chromate	-	-	-	-	10

Older Plant:

Dissolved Solids	103,090 (chlorides, hypochlorites)

Alkali Plant:

NaOH	25
NaCl	28.9 (added to seawater)

Hydrochloric Acid

Hydrochloric acid is manufactured principally by two processes: (1) As a by-product of organic chlorinations; and (2) By direct reaction of chlorine with hydrogen. Only production by direct reaction of chlorine is considered herein. In this process, hydrogen and chlorine are reacted in a vertical burner. The hydrogen chloride formed is condensed in an absorber from which it flows to a storage unit for collection and sale. The arrangement used at the exemplary facility (plant 121) is similar to the standard flow diagram shown in Section IV. The special waste treatment system used during startup of this facility startup is shown in Figure 42.

The raw waste loads from hydrochloric acid manufacture are presented below. Some of these are markedly dependent on conditions, with most of the wastes being produced during startups. There are no water-borne wastes during periods of normal operation.

Waste Products	Process Source	Amount of Product
1. Chlorine*	Burner Run - Chlorine-rich	Startup - 100 kg/kkg (200 lb/ton) avg. 5-200 range (10-400) Operation - 5 kg/kkg (10 lb/ton) avg. 0-10 range (0-20) Shutdown - no waste
2. HCl**	-	Startup - 4.5 kg/day (9 lb/ton) Operation - none Shutdown - none

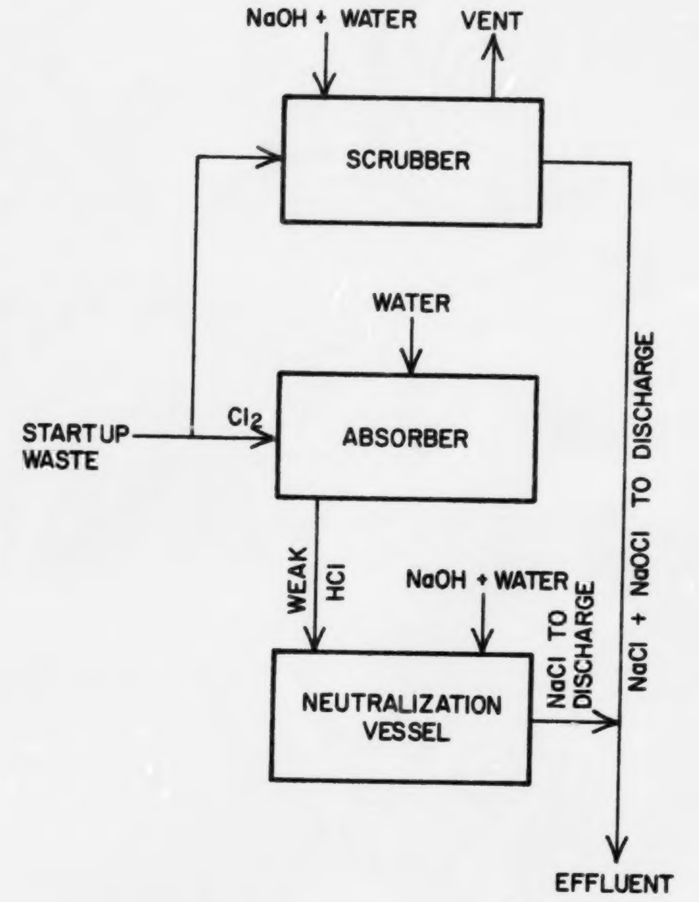
NaOH + WATER
VENT
SCRUBBER
WATER
STARTUP WASTE
Cl_2
ABSORBER
WEAK HCl
NaOH + WATER
NaCl TO DISCHARGE
NaCl + NaOCl TO DISCHARGE
NEUTRALIZATION VESSEL
EFFLUENT

FIGURE 42
STARTUP WASTE TREATMENT SYSTEM AT PLANT 121

3. NaOH*** reaction products (NaCl and NaOCl)	Neutralization	Startup - depends on HCl and Cl_2 to be neutralized Operation - none Shutdown - none

---

*Emerges in vent gas during normal operation, neutralized during startup by NaOH.

**All neutralized during startup.

***Caustic (NaOH) used has 12 percent NaCl present and is cell liquor from chlorine plant also in the complex.

All waste water treatment is performed during startup of the facility. During normal operation, there are no water-borne wastes to be treated. Water use at the facility is listed below:

A. Input

Type	Quantity cu m/day	Quantity l/kkg	Comments on Content
Lake	5,680 (150,000 gpd)	15,650 (3,750 gal/ton)	TDS-300 mg/l, SS-10 mg/l, Cl-65 mg/l, SO_4-34 mg/l, $CaCO_3$-200 mg/l, $Ca(HCO_3)_2$-2-250 mg/l.
Well	1,135 (30,000 gpd)	3,130 (750 gal/ton)	Same as lake water except lower in sulfate, low SS (less than 10 mg/l).

B. Water Use

Type	Quantity cu m/day	Quantity l/kkg	Percent Recycled
Cooling*	1,135 (30,000 gpd)	3,130 (750 gal/ton)	0
Process	760 (20,000 gpd)	2,085 (500 gal/ton)	0 (Leaves as part of product)
Disposal from neutralization tank**	4,545 (120,000 gpd)	12,520 (300 gal/ton)	0
Miscellaneous	380 (10,000 gpd)	1,040 (250 gal/ton)	0

---

*Phosphate treatment used for this water. About 0.5 mg/l excess phosphate is employed.

**For safety purposes, continuous water flow is maintained into the neutralization tank even during normal process operation when no effluent or NaOH are introduced.

The effluents from the process streams before sewer at plant 121 are listed below.

Waste Stream	cu m/day		1/kkg	
1. Neutralizing Reactor	4,355	(115,000 gpd)	12,000	(2,875 gal/ton)
2. Neutralizing Siphon Tank*	190	(5,000 gpd)	520	(125 gal/ton)
3. Test Sink and Washdown	380	(10,000 gpd)	1,040	(250 gal/ton)
4. Cooling Water	1,135	(30,000 gpd)	3,130	(750 gal/ton)

---

*Siphon Tank is 26,500 l and has less than 4 l/day drainage. It is operated batchwise with excess caustic always present. When the alkali content has been neutralized, it is disposed of.

After treatment, these streams are fed to a common equalization pond for pH adjustment and suspended solids removal prior to discharge. Effluent after this treatment (for the total complex) contains less than 10 mg/l of suspended solids and 2588 mg/l chlorides and sulfates, mostly from other processes.

The plant effluent characteristics are given below. There are no wastes during normal operation. All of the wastes arise from startup operations. In addition, there is an air-borne chlorine vent gas waste as noted earlier.

Parameter	Stream No. 1 Operation/Startup		Stream No. 2 Operation/Startup		Stream No. 3	Stream No. 4
Total Suspended Solids	10*mg/l	10 mg/l	No Effluent	Batch for a number of processes; 90-180 kg of Cl2 neutralized per month and disposed of in this stream	Same as lake water	
Total Dissolved Solids	300*mg/l	40,000-50,000				
BOD	**	10 mg/l				
COD	**	**				
pH	6.5-10.0 9 avg.	6.5-10.0 9 avg.				

---

*Same as lake water
**Undetectable

All of the chlorine-burning HCl plants are located within chlor-alkali complexes. At present, there are four such facilities.

The 121 plant was sampled because of two considerations: 1) Unlike the other facilities, hydrochloric acid wastes are easily segregable. At other plants these wastes are mixed with chlor-alkali wastes before treatment; and 2) Unlike some other facilities, there are no hydrochloric acid wastes during normal operations.

This facility could be further improved by: (1) More efficient scrubbing of process tail gases to remove chlorine and use of the resulting chloride/hydrochloric solutions elsewhere in the facility; and (2) Reuse of the sodium chloride formed by acid neutralization.

Hydrofluoric Acid

Hydrofluoric acid is manufactured by reaction of sulfuric acid with fluorspar ore (mainly calcium fluoride). The reaction mixture is heated and the hydrofluoric acid leaves the furnace as a gas, which is cooled, condensed and sent to a purification unit. There the crude hydrofluoric acid is redistilled and either absorbed in water to yield aqueous hydrofluoric acid or compressed and bottled for sale as anhydrous hydrofluoric acid.

At an exemplary plant (plant 152), the calcium sulfate byproduct from the reactor is slurried with water and sent to waste treatment. Also, all tail gases are scrubbed and the scrubber water is sent to the waste abatement system. Figure 43 shows a detailed process diagram for the exemplary facility, and Figure 44 shows the waste water recycling system in use at this plant.

The waste products from hydrofluoric acid manufacture are shown below. Wastes consist of materials from the furnaces, which include calcium sulfate, calcium fluoride and sulfuric acid, plus fluoride-containing scrubber wastes.

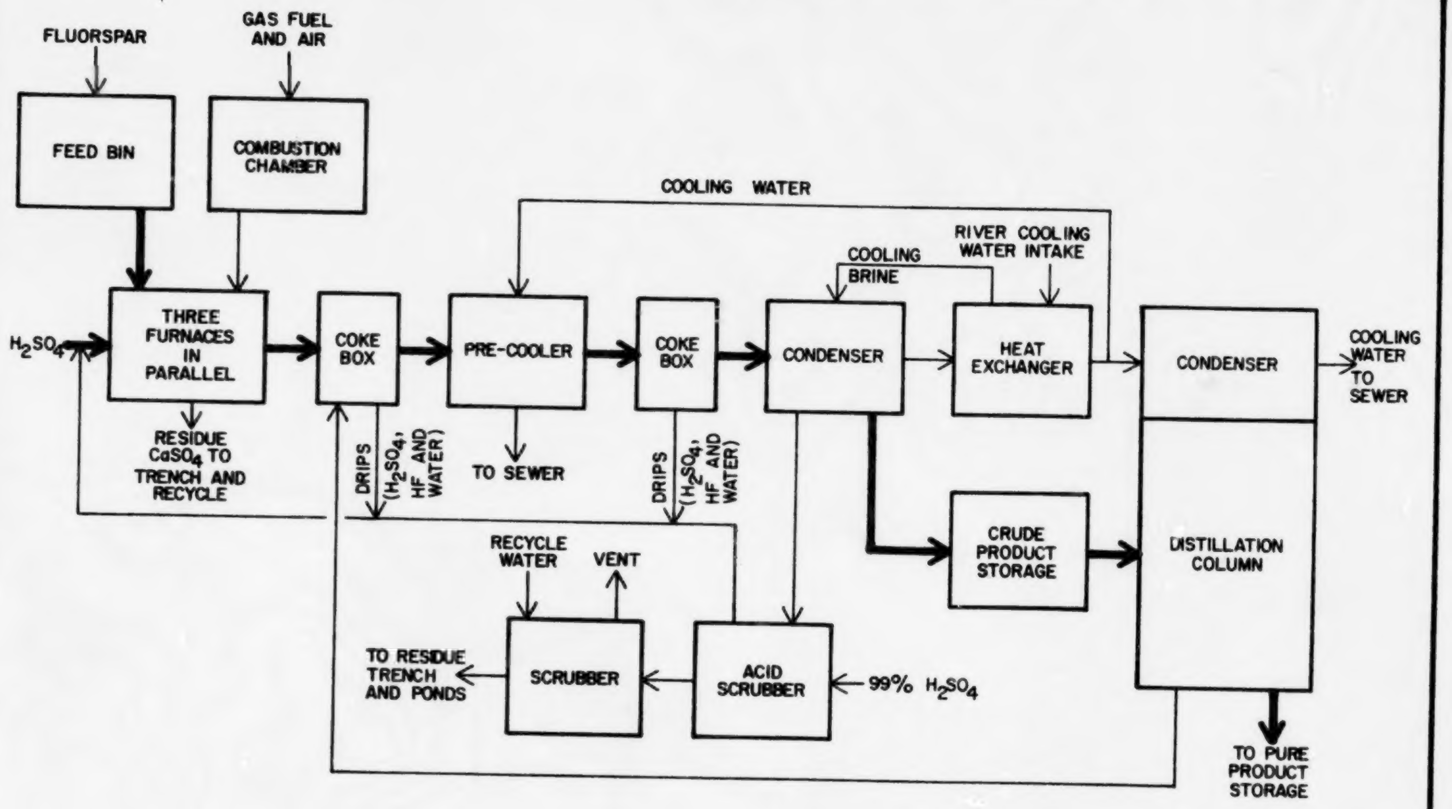
FLUORSPAR
GAS FUEL AND AIR
FEED BIN
COMBUSTION CHAMBER
COOLING WATER
RIVER COOLING WATER INTAKE
COOLING BRINE
H_2SO_4
THREE FURNACES IN PARALLEL
COKE BOX
PRE-COOLER
COKE BOX
CONDENSER
HEAT EXCHANGER
CONDENSER
COOLING WATER TO SEWER
RESIDUE $CaSO_4$ TO TRENCH AND RECYCLE
DRIPS (H_2SO_4, HF AND WATER)
TO SEWER
DRIPS (H_2SO_4, HF AND WATER)
CRUDE PRODUCT STORAGE
DISTILLATION COLUMN
RECYCLE WATER
VENT
TO RESIDUE TRENCH AND PONDS
SCRUBBER
ACID SCRUBBER
99% H_2SO_4
TO PURE PRODUCT STORAGE

FIGURE 43
HYDROFLUORIC ACID PROCESS FLOW DIAGRAM OF PLANT 152

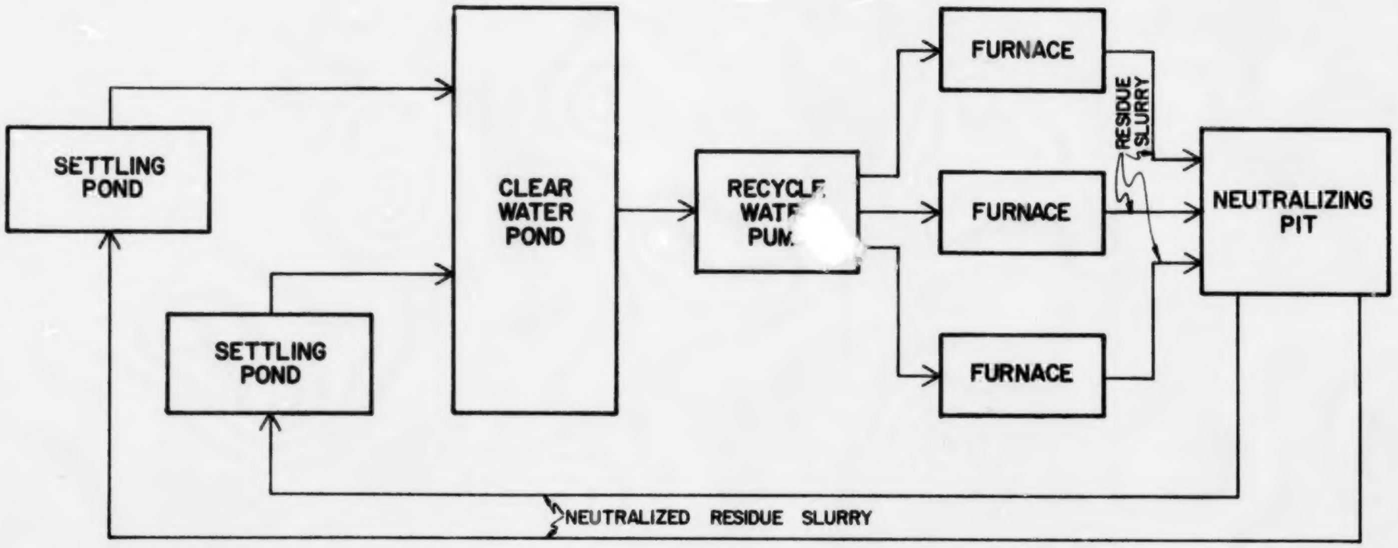
SETTLING POND
SETTLING POND
CLEAR WATER POND
RECYCLE WATE PUM
FURNACE
FURNACE
FURNACE
RESIDUE SLURRY
NEUTRALIZING PIT
NEUTRALIZED RESIDUE SLURRY

FIGURE 44
EFFLUENT RECYCLE SYSTEM AT PLANT 152

Waste Product	Process Source	Avg. kg/kkg (lb/ton) of Product
1. $CaSO_4$	Kiln (reactor)	3,620 (7,240)
2. H_2SO_4	Kiln (reactor)	110 (220)
3. CaF_2	Kiln (reactor)	63 (126)
4. HF	Kiln (reactor)	1.5 (3)
5. H_2SiF_6	Scrubber	12.5 (25)
6. SiO_2	Kiln (reactor)	12.5 (25)
7. SO_2	Scrubber	5 (10)
8. HF	Scrubber	1 (2)

The water use within plant 152 is shown below.

Type	Total Quantity		Recycled
	cu m/day (gpd)	l/kkg (gal/ton)	
Cooling (river water)	3,270 (864,000)	90,140 (21,600)	0 percent
Slurry and Scrubber	3,270 (864,000)	90,140 (21,600)	100 percent

All process and scrubber waste waters are recycled in the exemplary plant. The waters used to slurry and remove the calcium sulfate from the furnaces and scrubber waters are fed to a pond system after being treated with caustic or soda ash and lime to precipitate fluorides and adjust the pH. In the pond system, the insolubles are settled out and the waters are then reused in the process as shown in Figure 44.

Only cooling water is discharged from this facility. Table 11 shows the compositions of process waters before and after neutralization and of the river intake water which is essentially the same as the cooling water effluent. Low fluoride levels are easily maintained because of segregation of discharged cooling waters from the process water.

Verification measurements, shown for the plant intake water and the outflow of cooling water, are given in Table 12. The similarity of the intake and cooling water discharge verifies that there is no process water leakage into the cooling stream, and, therefore, there is no process water discharge from this exemplary hydrofluoric acid manufacturing plant.

Hydrogen Peroxide

Hydrogen peroxide is manufactured by three different processes: (1) An electrolytic process; (2) An organic process involving the oxidation and reduction of anthraquinone; and (3) A by-product of acetone manufacture from isopropyl alcohol. In this study, only the first two processes were considered.

TABLE 11. Intake Water and Raw Waste Composition Data at Plant 152*

Parameters		Units	Raw Waste Into Treatment	Recycle Water From Treatment	Intake River Water
Aluminum	Al	µg/l	7400	2200	2600
Beryllium	Be	"	66	64	20
Calcium	Ca	mg/l	640	450	12.2
Cadmium	Cd	µg/l	16	12	2
Cobalt	Co	"	300	280	26
Chromium	Cr	"	46	22	4
Copper	Cu	"	44	28	4
Iron	Fe	"	3100	780	1060
Magnesium	Mg	mg/l	6.0	6.4	3.2
Manganese	Mn	µg/l	100	106	68
Molybdenum	Mo	"	56	56	26
Nickel	Ni	"	80	68	4
Lead	Pb	"	1320	3400	820
Titanium	Ti	"	240	220	20
Zinc	Zn	"	1100	880	440
Barium	Ba	"	740	1020	1280
Potassium	K	mg/l	6.4	8.6	0.6
Sodium	Na	"	490	660	4.2
Tin	Sn	µg/l	140	140	24
Ammonia-Nitrogen		mg/l N	0.23	0.05	0.23
COD		" O2	13.4	-	-
Fluoride		" F	13.0	12.5	0.2
Total Suspd Solids		"	16596	59	21
Total Solids		"	22015	3758	124
Total Vol. Solids		"	1220	340	58
Total Dissolved Solids		"	4250	3572	132
Nitrate		mg/l N	0.26	0.20	0.13
Nitrite		"	0.02	0.01	0.20
Nitrogen-Kjeldahl		"	0.57	0.46	0.46
Phosphate Total		mg/l P	1.60	0.96	0.02
Sulfate		mg/l S	880	767	7
Arsenic		µg/l	77	49	74
pH		-	3.86	7.22	7.17
TOC		mg/l	4	6	5

---

*Data furnished by manufacturer

TABLE 12. Comparison of Plant Intake Water and Cooling Water Discharge at Plant 152*

Parameter		Intake	Discharge	Units
Flow		Not Measured	3,270 (864,000)	cu m/day (GPD)
Temperature		Not Measured	18 (64)	°C (°F)
Color (Apparent)		50	50	Units APHA
Turbidity		19	19	FTU
Conductivity		65	65	mg/l NaCl
		135	135	micromhos/cm
Suspended Solids		7	12	mg/l
pH		7.40	7.50	-
Acidity: Total		0	0	mg/l $CaCO_3$
Free		0	0	mg/l $CaCO_3$
Alkalinity (Total)	P	0	0	mg/l $CaCO_3$
	T	0	30	mg/l $CaCO_3$
Hardness: Total		50	50	mg/l $CaCO_3$
Halogens: Chlorine		0	0	mg/l Cl_2
Fluoride		0.2	0.2	mg/l F^-
Sulfate		25	22	mg/l SO_4^{-2}
Nitrogen (Total)		0.20	0.14	mg/l N
Heavy Metals:				
Iron		0.25	0.25	mg/l Fe
Chromate (Cr+6)		0.02	0.02	mg/l Cr^{+6}
Oxygen (Dissolved)		11	10.4	mg/l O_2
COD		25	0	mg/l

---

*Data from verification sampling

a) Organic process

In the organic process, anthraquinone (or an alkylanthraquinone) in an organic solvent is catalytically hydrogenated to yield a hydroanthraquinone. This material is then oxidized with oxygen or air back to anthraquinone, with hydrogen peroxide being produced as a by-product. The peroxide is water-extracted from the reaction medium, and the organic solvent and anthraquinone are recycled. The recovered peroxide is then purified and shipped. Figure 45 shows a specific flowsheet for plant 069, including part of the waste abatement program.

Waste Products	Process Source	Operation Avg. Range kg/kkg (lb/ton)
Sulfuric Acid	Ion Exchange Units	12.5-15 (25-30)
Trace Organics	Contact Cooling	0.17-0.35 (0.34-0.70)
Hydrogen Peroxide	Purification Washings	20-25 (40-50)

The process runs continuously, except for shut-down approximately 10 days/year. Total discharge will normally be no higher during start-up and shut-down periods than under operation at capacity.

Well water at 312 cu m/kkg of product (74,500 gal/ton) having the following composition in the water input at plant 069.

Total Solids	110-125 mg/l
Carbon Dioxide	30-60 mg/l
Total Hardness	80-100 mg/l
Fe	1-3 mg/l
Cu	0.03-0.06 mg/l
Zn	0.02 mg/l
Sulfate	2-7 mg/l
Alkalinity ($CaCO_3$)	70-110 mg/l

Water Usage

Type	cu m/kkg (gal/ton)	% Recycled
Cooling	365 (87,200)	25 percent recycled 35 percent of remainder used twice
Process	16 (3,800)	----

Most of the water is used for cooling, and a relatively large fraction of this water is recycled.

The data below describes the treatment of the waste stream emerging from the peroxide plant. Peroxide is decomposed by iron filings, and organic solvent losses are minimized by a skimming operation:

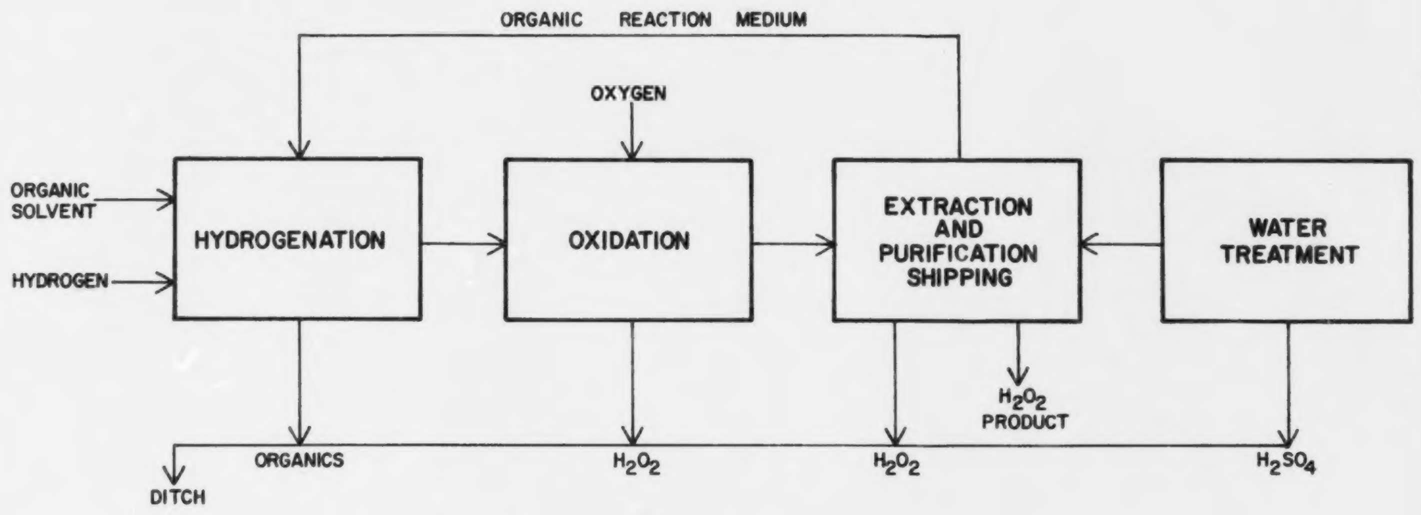
ORGANIC REACTION MEDIUM
OXYGEN
ORGANIC SOLVENT
HYDROGEN
HYDROGENATION
OXIDATION
EXTRACTION AND PURIFICATION SHIPPING
WATER TREATMENT
H_2O_2 PRODUCT
DITCH
ORGANICS
H_2O_2
H_2O_2
H_2SO_4

FIGURE 45
HYDROGEN PEROXIDE PROCESS DIAGRAM FOR PLANT 069

Waste Stream	Source	cu m/kkg (gal/ton)	Treatment	Final Disposal
Process Effluent	Process	294 (70,200)	1. Peroxide reacted with iron filings 2. Skimmers used to trap organics for recovery 3. Waste sulfuric acid is collected and discharged at a controlled rate 4. Solids (alumina & carbon) are hauled to landfill	River

The effectiveness of the treatments in use is:

Method	Qualitative Rating	Waste Reduction Accomplished
Reduction	Generally satisfactory	80 percent reduction of peroxide to water and oxygen
Skimming	Generally satisfactory	60-70 percent of organics recovered

The effluent composition after treatment is given in Table 13. The wastes consist of unreacted peroxide and a small amount of organics and sulfates.

b) Electrolytic process

In the electrolytic process, a solution of ammonium bisulfate is electrolyzed. Hydrogen is liberated at the cathodes of the cells used, and ammonium persulfate is formed at the anode. The persulfate is then hydrolyzed to yield ammonium bisulfate and hydrogen peroxide which is separated from the solution by fractionation. The ammonium bisulfate solution is then recycled, and the peroxide is recovered for sale. The only waste is a stream of condensate from the fractionation condenser. Figure 46 shows the process waste treatment system at plant 100.

Table 14 lists the raw wastes from peroxide manufacture at plant 100. These consist of ammonium bisulfate losses, ion exchange losses, boiler blowdowns and some cyanide wastes from the special batteries used in electrolysis.

Plant water intake and use are as follows:

TABLE 13. Plant 069 Process Water Effluent After Treatment

	Plant Data		Verification Sample	
Parameter*	Average	Range	Verification Measurement	Plant 069 Measurement
Total Suspended Solids	-	15-20	9	9
Total Dissolved Solids	-	310-330	98	117
BOD	-	6-7	-	-
COD	40	-	50	33
pH	-	6-9	6.4	6.6
Temperature	30°C	-	27°C	-
T.O.C.	-	5-15	-	-
Hydrogen Peroxide	-	60-80	-	37.8
Turbidity (Jackson Units)	25	-	12	25
Color (APHA Units)	-	20-20	50	10
Acidity (Free)	-	40-50	-	46
Acidity (Total)	0	-	-	-
Alkalinity (Total)	-	150-195	61	-
Hardness (Total)		90-105	92	-
Chloride	2	-	5	7
Sulfate	-	40-75	43	52
Iron	-	2-3.5	1.6	0.26
Copper	-	0.08-0.09	-	-
Flow	25,000 cu m/day (6.6 MGD)	-	26,000 cu m/day (7.1 MGD)	-

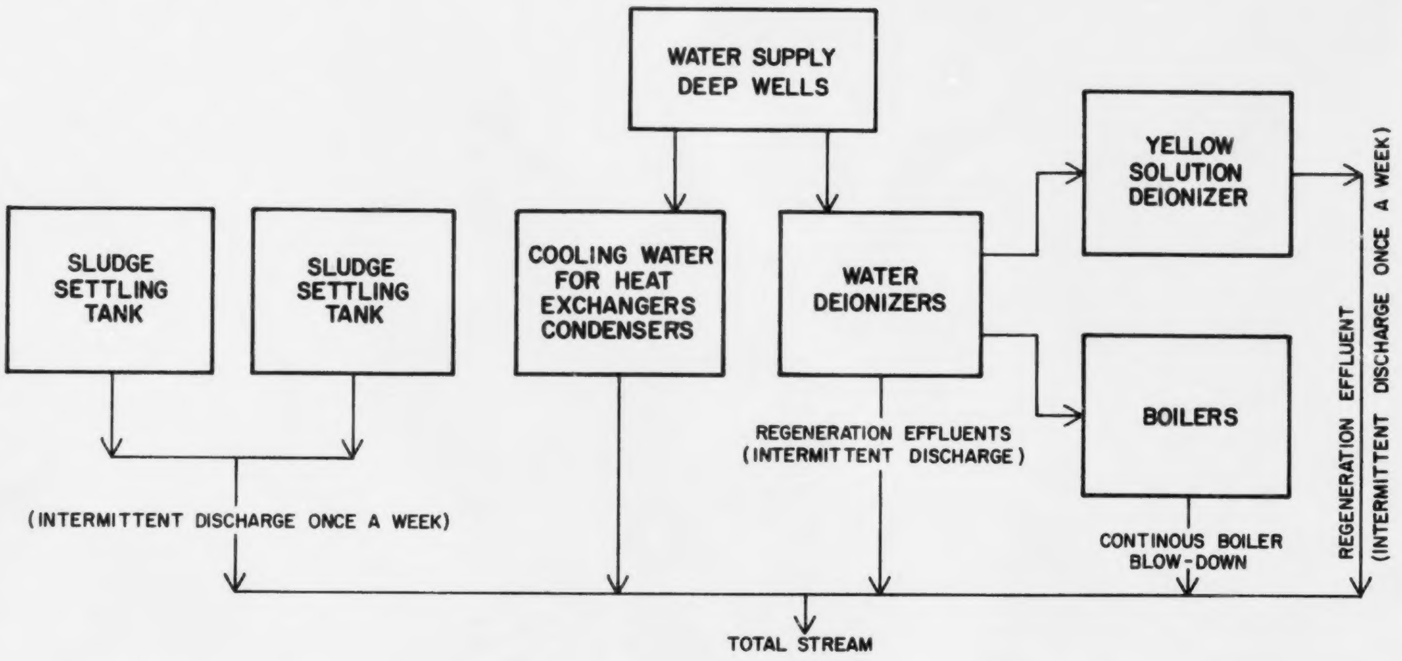
WATER SUPPLY DEEP WELLS
SLUDGE SETTLING TANK
SLUDGE SETTLING TANK
COOLING WATER FOR HEAT EXCHANGERS CONDENSERS
WATER DEIONIZERS
YELLOW SOLUTION DEIONIZER
BOILERS
(INTERMITTENT DISCHARGE ONCE A WEEK)
REGENERATION EFFLUENTS (INTERMITTENT DISCHARGE)
CONTINOUS BOILER BLOW-DOWN
REGENERATION EFFLUENT (INTERMITTENT DISCHARGE ONCE A WEEK)
TOTAL STREAM

FIGURE 46
SCHEMATIC SHOWING WASTE SOURCES AND DISCHARGE AT PLANT 100

TABLE 14. Raw Waste Loads at Plant 100

		kg/kkg of Peroxide (lb/ton)	
Waste Product	Process Source	Operation	Startup Shutdown
1. Blue prussiate sludge	Purif.	0.18(0.36)	No significant difference during startup & shutdown periods. Plant runs continuously; shuts down once per year.
2. Gray sludge	Battery rebuild	(5 times per year)	
3. Ion Exchange sludge	Deionizer regen.	---	
4. H_2SO_4	Plant solution loss	0.0018(0.0036)	
5. $(NH_4)_2SO_4$	Plant solution loss	0.012(0.024)	
6. Water flow	Cooling	2000-2900 (4000-58000)	
7. HCl	Deionizer regen.	1.3(2.6)	
8. NaOH	Deionizer regen.	0.33(0.66)	
9. Steam condensate	Boiler blowdown	581(1162)	

Comments: H_2SO_4 and $(NH_4)_2SO_4$ are used to replenish plant solution. $Na_4Fe(CN)_6$ is converted to $(NH_4)_4Fe(CN)_6$ through ion exchange (yellow solution).
NH_4SCN is oxidized in the batteries and is used for better current efficiency.
HCl and NaOH are used for regeneration of demineralized water ion exchange resins.

Water	Flow, cu m/day (mgd)	Amount, l/kkg (gal/ton)	Use
Municipal	7.2 (0.0019)	601 (114)	Drinking, Washing, Sanitary
Well	41,600 (11.0)	3,480,000	76 cu m/day (0.002 mgd) demineralized for process water, rest used as cooling

Of the 76 cu m/day of process water, 31 percent is used in the product. Recycle flow of process water is 132 cu m/day and recycle flow of steam is 305 cu m/day (liquid basis). About 26.5 cu m/day is boiler blowdown. None of the cooling water is recycled. Table 15 lists the various plant effluent streams, their sources, flows and treatments. Treatments consist of ion exchange for pH control and recovery of some process materials, and recovery of platinum in the waste streams. After this, wastes are discharged.

Performance information on the pH control and ion exchange technology used for waste abatement in this plant is:

Method	Qualitative Rating	Waste Reduction Accomplished
1. pH Control	Good	99+ percent
2. Process change	Excellent	CN- load reduced 98 percent - Additional concentration to discharge stream less than 0.01 mg/l
3. Monitoring	Good	Reduces unknown discharges and allows quick operation response.

Table 16 lists the compositions of the various effluent streams after treatment. These streams are mixed prior to discharge. Table 17 shows an analysis of the intake water and final effluent after mixing. Only very small amounts of materials are introduced into the waters used, and cyanides in the effluent are negligible.

Nitric Acid

Nitric acid is manufactured from ammonia by a catalytic oxidation process. Ammonia is first catalytically oxidized to nitric oxide, which is then further oxidized to nitrogen dioxide. The nitrogen dioxide is then reacted with water under pressure to yield nitric acid. Plant 114 manufactures only commercial 63

TABLE 15. Effluent Treatment Data for Plant 100

A. Water Streams

Stream No.	Source	l/day (MGD)	l/kkg (gal/ton)
1. Low Exchange Regenerant	Demineralizer	3,790(1,000)	317(76)
2. Blue Prussiate Supernatant (filter backwash)	Filters	568(150)*	47.6(11.4)
3. Yellow Solution	Ion Exchange	568(150)*	47.6(11.4)
4. Boiler Blowdown	Boilers	26,500(7,000)	2,210(530)

B. Treatments

Stream No. (same as above)	Treatment Method	Final Disposal System
1	Anion and cation regenerants are mixed to control pH and slowly released.	Plant effluent
2	Settled for platinum recovery, siphoned and filtered**.	Plant effluent
3	Backwash recycled to process and regenerant is discharged.	Plant effluent
4	Dilution	Plant effluent

---

*These operations are batch carried out an average of once per week.

**Sludges recovered here are sent to refiners for recovery of platinum values.

TABLE 16. Composition of Plant 100 Effluent Streams After Treatment*

Constituents	No. 1 Stream	No. 2 Stream	No. 3 Stream	No. 4 Stream
Total Suspended Solids	1856 as $CaCO_3$ equiv. during regeneration	--	0	--
Total Dissolved Solids	Comparable to raw water	200-400	40,000	1,000
BOD	Same as raw water	--	--	--
COD	Same as raw water	--	--	--
pH	6.5-8.5	4	7	8
Temperature, °C	17	18	18	--
Conductivity micromhos/cm	7160	--	--	--
Alkalinity	--	--	--	400
Free Cyanide	--	<2	<2	0
Phosphate	--	--	--	30
Chloride	--	--	--	20-30 (as NaCl)

---

*all units mg/l unless otherwise specified.

TABLE 17. Plant 100 Water Intake and Final Effluent Verification Measurements

Parameter*	Well Water	Outfall
Conductivity, micromhos/cm	120 (as NaCl) 240	120 (as NaCl) --
Color	0	0
Turbidity	0	0
SS	0	0
pH	6.88	7.04
Sulphate	18	21
Nitrate	3.3	2.3
Phosphate	0.35	0.36
Iron	0.02	0.01
Chloride	6.5	7.5
Hardness (Ca)	65	70
Total Hardness	95	90

---

*mg/l unless otherwise specified.

percent nitric acid. Fuming (i.e., more than 70 percent) nitric acid and nitrogen pentoxide are made only at a few facilities and are not covered in this report. The flow diagram for plant 114 is given in Figure 47.

The raw waste load from nitric acid production at Plant 114 is listed below. The waste values are not affected by startup or shutdown. There are no nitrates in the waste. All weak nitric acid lost in the manufacturing process is recycled to the process at this facility. The wastes consist only of water treatment chemicals used for the cooling water.

Waste Products	Process Source	Avg. kg/kkg HNO_3(lb/ton)
1. Lime	Boiler Feedwater	0.47 (0.94)
2. Calcium and Magnesium Carbonates	Boiler Feedwater	0.6 (1.2)
3. Disodium Phosphate	Boiler	0.0016 (0.0032)
4. Sodium Sulfate	Boiler	0.0008 (0.0016)
5. Sulfuric Acid	Cooling Tower	0.0016 (0.0032)
6. Chlorine	Cooling Water Treatment	1.0 (2.0)

Plant water use is shown below and describes the large amount of water and weak acid recycling at the plant. Only cooling water is discharged, and this waste stream is currently untreated.

A. Water Inputs

Types	Quantity cu m/day	Quantity l/kkg
Well	3,815 (1,008,000 gpd)	13,150 (3,150 gal/ton)

B. Water Use

Water Use	Quantity cu m/day	Quantity l/kkg	Recycled
Cooling	31,000 (8,000,000 gpd)	106,800 (25,000 gal/ton)	95
Process stream	775 (200,000 gpd)	2,670 (6,250 gal/ton)	100

The plant effluent streams are shown below. Wastes discharged are only water treatment chemicals.

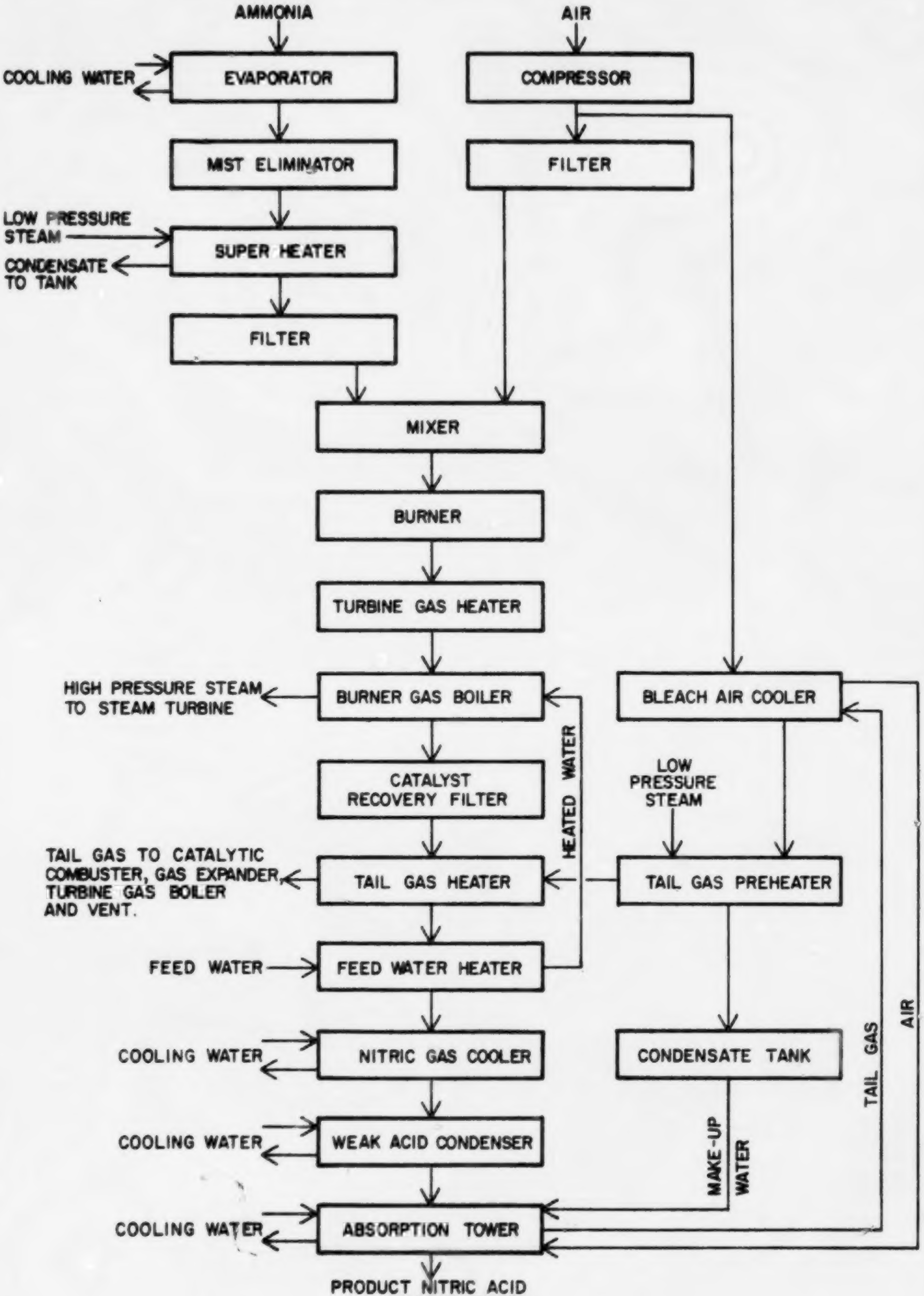
AMMONIA
AIR
COOLING WATER
EVAPORATOR
COMPRESSOR
MIST ELIMINATOR
FILTER
LOW PRESSURE STEAM
SUPER HEATER
CONDENSATE TO TANK
FILTER
MIXER
BURNER
TURBINE GAS HEATER
HIGH PRESSURE STEAM TO STEAM TURBINE
BURNER GAS BOILER
BLEACH AIR COOLER
HEATED WATER
CATALYST RECOVERY FILTER
LOW PRESSURE STEAM
TAIL GAS TO CATALYTIC COMBUSTER, GAS EXPANDER, TURBINE GAS BOILER AND VENT.
TAIL GAS HEATER
TAIL GAS PREHEATER
FEED WATER
FEED WATER HEATER
COOLING WATER
NITRIC GAS COOLER
CONDENSATE TANK
TAIL GAS
AIR
COOLING WATER
WEAK ACID CONDENSER
MAKE-UP WATER
COOLING WATER
ABSORPTION TOWER
PRODUCT NITRIC ACID

FIGURE 47
NITRIC ACID PROCESS FLOW DIAGRAM
FOR PLANT 114

Sources	cu m/day	l/kkg
Boiler Feedwater Treatment	5 (1,250 gpd)	16 (3.9 gal/ton)
Boiler Blowdowns	30 (7,800 gpd)	85 (24.4 gal/ton)
Cooling Water Blowdowns	3600 (95,000 gpd)	1240 (297.0 gal/ton)

(All streams tie into common effluent header before discharge)

Because of recycling of some water and of all nitrogen-containing streams, this plant is exemplary. However, as in many other cases, cooling waters are untreated prior to discharge. The plant effluents are listed below.

	Average	Range	Units
Total Suspended Solids	80	50-100	mg/l
Total Dissolved Solids	239	200-250	mg/l
BOD	5	-	mg/l (O2)
COD	10	-	mg/l (O2)
pH	7.8	7.5-8.5	-
Temperature	25	24-27	°C
Turbidity	125	-	JTU
Color	330	-	PTCO
Conductivity	500	-	mhos
Alkalinity (Total)	300	-	mg/l
Hardness (Total)	300	-	mg/l
Chloride	18	-	mg/l
Fluoride	0.2	-	mg/l
Sulfite	0.2	-	mg/l
Sulfate	60	-	mg/l
Phosphates	0.4	-	mg/l
Nitrate	0.2	-	mg/l
Iron	7.5	-	mg/l
Manganese	0.2	-	mg/l

A plant visit verified that only cooling water is discharged from plant 114.

Potassium Metal

For the commercial preparation of potassium metal (K), potassium chloride is melted in a gas-fired melt pot and fed to an exchange column. The molten potassium chloride flows down over steel Raschig rings in the packed column, where it is contacted by ascending sodium vapors coming from a gas-fired reboiler. An equilibrium is established between the two, yielding sodium chloride and elemental potassium as the products. The sodium chloride formed is continuously withdrawn at the base of the apparatus and is normally sold. The column operating conditions may be varied to yield either pure potassium metal as an overhead product or to vaporize sodium along with the potassium to produce sodium potassium (NaK) alloys of varying compositions. Potassium metal of over 99.5 percent purity can be continuously produced by this process.

Production of potassium in the United States was about 90 kkg (100 ton) in 1972, essentially all of it originating from one facility - plant 045. Contacts with this manufacturer have revealed that the process diagram accurately describes their process. No process water is used and there are no waterborne effluents.

Potassium Dichromate

Potassium dichromate is prepared by reaction of potassium chloride with sodium dichromate. Potassium chloride is added to the dichromate solution, which is then pH-adjusted, saturated, filtered and vacuum cooled to precipitate crystalline potassium dichromate. The product is recovered by centrifugation, dried, sized and packaged. The mother liquor from the product centrifuge is then concentrated to precipitate sodium chloride which is removed as a solid waste from a salt centrifuge. The process liquid is recycled back to the initial reaction tank.

The raw wastes from potassium dichromate manufacture are listed below. These are crystalline sodium chloride and filter aids which are solid wastes and are hauled away for landfill disposal by a contractor.

Waste Products	Process Source	kg/kkg of Product (lb/ton)
NaCl	Centrifuge	400 (800)
Filter aid	Filter	0.85 (1.7)

Exemplary plant water usage is given below. All process waters are recycled. The only wastes currently discharged emanate from contamination of once-through cooling water used on the barometric condensers on the product crystallizer. Plant 002 has plans to replace the barometric condensers with heat exchangers using non-contact cooling water. This should eliminate the hexavalent chromium waste completely. With this change, no process waste waters will be discharged.

A. Water Inputs to Plant

Type	Quantity cu m/day	Quantity l/kkg	Comments
River	1,325 (350,000 gpd)	97,200 (23,300 gal/ton)	Untreated except for macrofiltration
Municipal	245 (65,000 gpd)	18,100 (4,330 gal/ton)	Untreated

B. Water Usage

Type	Quantity cu m/day	Quantity l/kkg	Recycle
Cooling	1,325 (350,000 gpd)	97,200 (23,300 gal/ton)	0
Process (makeup)	245 (65,000 gpd)	18,100 (4,330 gal/ton)	100

Presently, the only effluent from this plant is cooling water, possibly contaminated with hexavalent chromium in the barometric condenser. Replacement of the condenser with a non-contact heat exchanger will eliminate cooling water contamination, although a larger amount of water will have to be used for the less efficient non-contact heat exchanger.

Potassium Sulfate

The bulk of the potassium sulfate manufactured in the United States is prepared by reaction of potassium chloride with dissolved langbeinite ore (potassium sulfate-magnesium sulfate). The langbeinite ore is mined and crushed and then dissolved in water to which potassium chloride is added. Partial evaporation of the solution produces selective precipitation of potassium sulfate which is recovered by centrifugation or filtration from the brine liquor, dried and sold. The remaining brine liquor is either discharged to an evaporation pond, reused as process water or evaporated to dryness to recover magnesium chloride. The fate of the brine liquor is determined by the saleability of the magnesium chloride by-product (depending on ore quality) and the cost of water to the plant. A diagram for the process used at plant 118 is given in Figure 48.

The table below presents a list of the raw wastes expected for potassium sulfate manufacture:

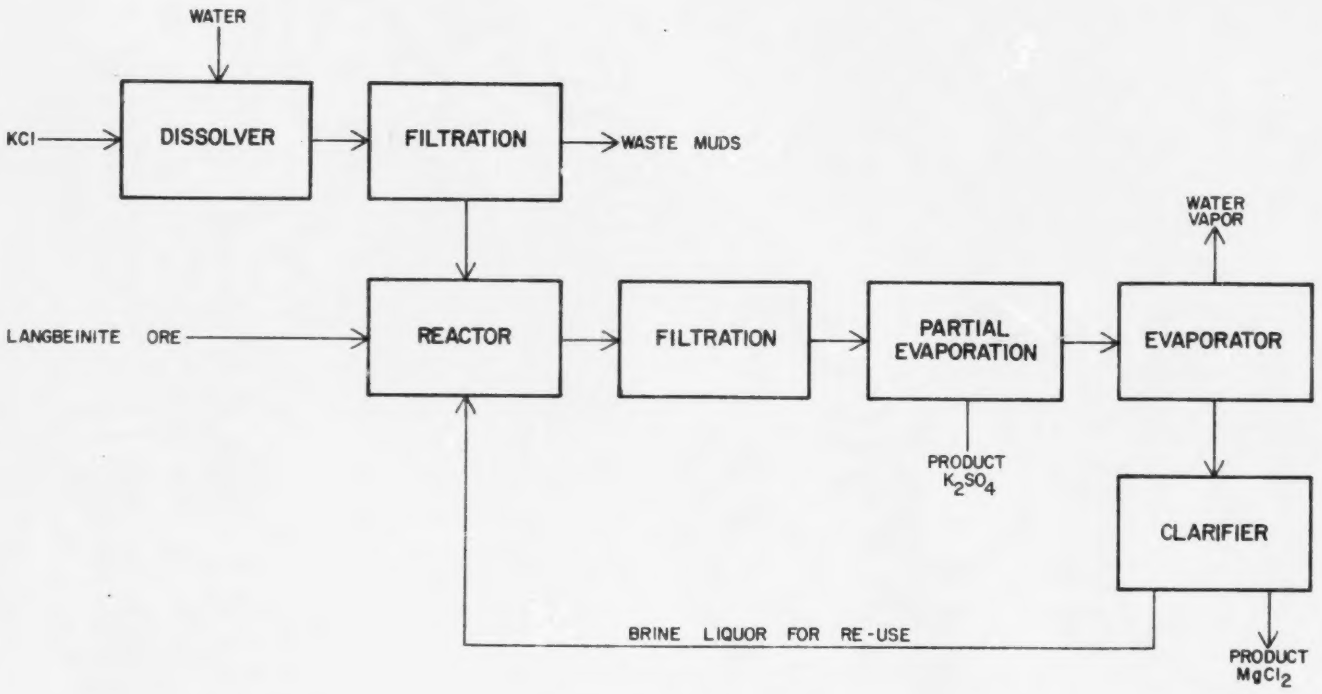
WATER
KCl
DISSOLVER
FILTRATION
WASTE MUDS
LANGBEINITE ORE
REACTOR
FILTRATION
PARTIAL EVAPORATION
EVAPORATOR
WATER VAPOR
PRODUCT K_2SO_4
CLARIFIER
BRINE LIQUOR FOR RE-USE
PRODUCT $MgCl_2$

FIGURE 48
POTASSIUM SULFATE PROCESS DIAGRAM AT PLANT 118

Waste Product	Process Source	kg/kkg of Product (lb/ton) Average	 Range
Muds, (silica, alumina, clay and other insolubles)	Dissolution of langbeinite ore	15-30 (30-60)	-
Brine liquor (Saturated magnesium chloride solution)	Liquor remaining after removal of potassium sulfate	-	0-2000*

---

*Part of the magnesium chloride is recovered for sale and part of the remaining brine solution is recycled for process water.

The high value corresponds to the case of no recycle or recovery of magnesium chloride. These brines contain about 33 percent solids. The wastes consist of muds from the ore dissolution and waste magnesium chloride brines and are not affected by startup or shutdown. The latter brine can sometimes be used for magnesium chloride production if high grade langbeinite ore is used. Composition of the brine solutions after potassium sulfate recovery is:

Potassium	3.2 percent
Sodium	1.3 percent
Magnesium	5.7 percent
Chloride	18.5 percent
Sulfate	4.9 percent
Water	66.7 percent

The amount of brine produced is about 650 kg of solids/kkg of potassium sulfate (1300 lb/ton) after evaporation. For higher grade ores, the sodium content is lower. The data presented above were supplied by plant 118.

The muds listed above are separated from the brine solutions at this exemplary plant by filtration after dissolution of the langbeinite ore. These are recovered and disposed of as landfill on the plant site. The brine wastes, containing mostly magnesium chloride, are either disposed of or treated in three different manners:

1. Evaporation with recovery of magnesium chloride for sale. This is practiced only when high grade ores are processed.
2. Reuse of the brine solution in the process in place of using process water. This is normally done to a considerable extent.
3. Disposal of the brines in evaporation pits.

At plant 118, all three of the above options are practiced, depending on the quality of the ore being processed.

Water use at plant 118 is described below:

Water Inputs:

Type	Quantity		Water Purity
	cu m/day (mgd)	l/kkg (gal/ton)	
Well Water	3,790 (1.0)	8,360 (2,000)	40 mg/l total solids

Water Flows:

Type	Quantity		Percent Recycled
	cu m/day (mgd)	l/kkg (gal/ton)	
Cooling	13,600 (3.6)	30,000 (7,200)	60-70 percent (remainder evaporated)
Process	2,270 (0.6)	5,010 (1,200)	67 percent recycled, 33 percent lost either by evaporation or removal from system with product or by-product.

There are no effluent streams from the plant since much of the water is recycled. Most of the water losses occur during the process evaporation steps.

Sodium Bicarbonate

Sodium bicarbonate is manufactured by the reaction of soda ash and carbon dioxide in solution. The product bicarbonate is separated by thickening and centrifugation and is then dried, purified and sold. A detailed process diagram for plant 166 is given in Figure 49. This facility is located within a Solvay process complex.

A listing of raw wastes produced in bicarbonate manufacture at plant 166 is shown below. These consist of unreacted soda ash, solid sodium bicarbonate, boiler wastes and ash from power generation equipment. The ash is treated as a solid waste.

Waste Product	Process Source	kg/kkg of Product (lb/ton)	
		Average	Range
1. Na_2CO_3	Slurry thickener overflow	38.0 (76.0)	0-375 (0-750)
2. Ash	Power generation	17.9 (35.8)	
3. Water purif. sludge	Boiler feed water purification	0.3 (0.6)	
4. $NaHCO_3$	Slurry thickener overflow	10.0 (20.0)	

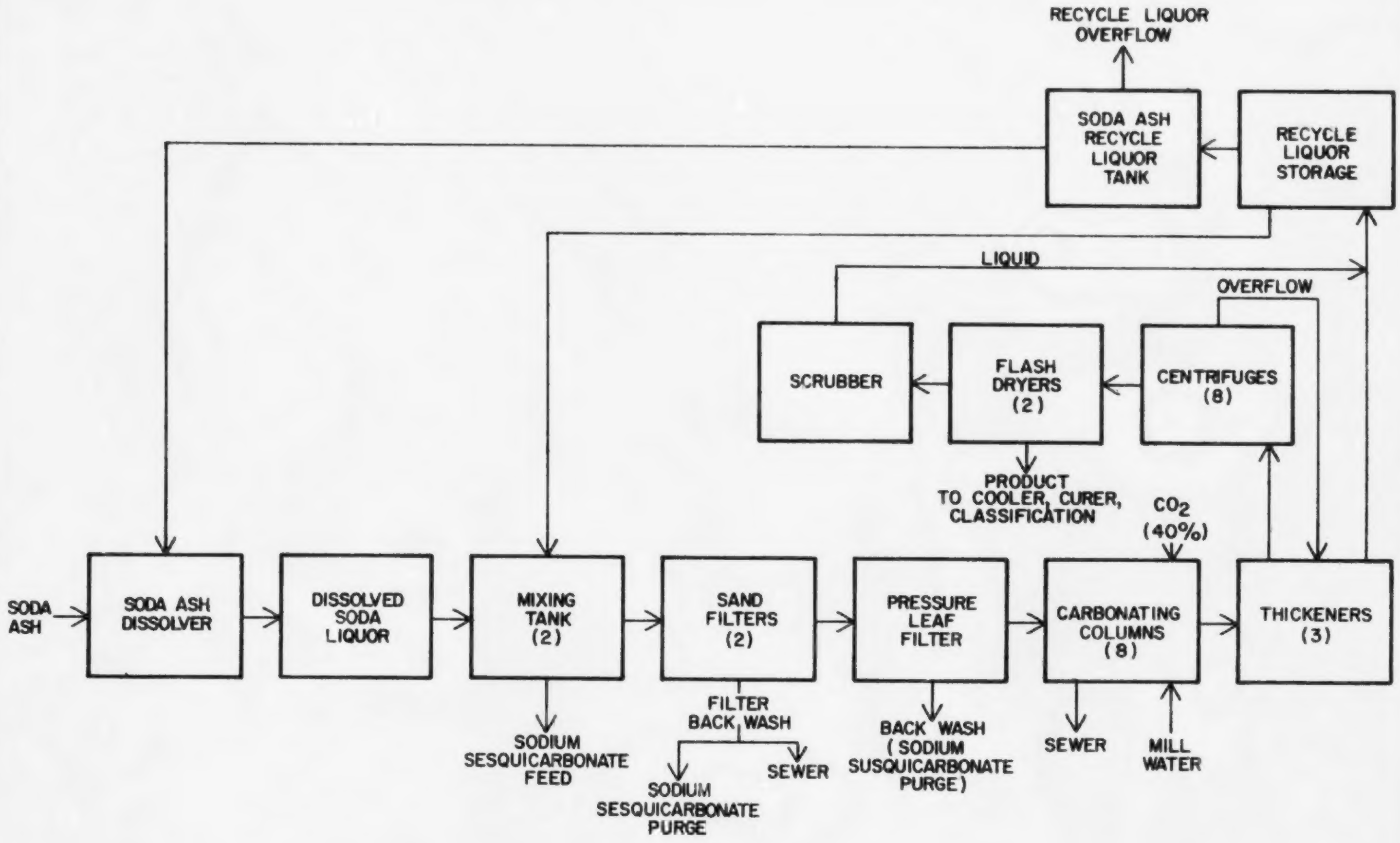
RECYCLE LIQUOR OVERFLOW
SODA ASH RECYCLE LIQUOR TANK
RECYCLE LIQUOR STORAGE
LIQUID
OVERFLOW
SCRUBBER
FLASH DRYERS (2)
CENTRIFUGES (8)
PRODUCT TO COOLER, CURER, CLASSIFICATION
CO2 (40%)
SODA ASH
SODA ASH DISSOLVER
DISSOLVED SODA LIQUOR
MIXING TANK (2)
SAND FILTERS (2)
PRESSURE LEAF FILTER
CARBONATING COLUMNS (8)
THICKENERS (3)
SODIUM SESQUICARBONATE FEED
FILTER BACK WASH
SODIUM SESQUICARBONATE PURGE
SEWER
BACK WASH (SODIUM SUSQUICARBONATE PURGE)
SEWER
MILL WATER

FIGURE 49
SOLVAY SODIUM BICARBONATE PROCESS FLOW DIAGRAM AT PLANT 166

The quantity of slurry thickener overflow depends upon the operation of another plant utilizing this by-product. The overflow is not constant, and occurs only when the sister plant mentioned above cannot absorb the entire flow. Consequently, the value shown above is based on an annual average, with a wide variation in flow over the period.

The water usage at plant 166 is shown below. Most of it is used for cooling purposes.

Water Inputs to Plant:

Type	cu m/day (mgd)	l/kkg (gal/ton)	Treatment
Lake	1,430 (0.378)	5,430 (1,300)	Chlorinated prior to use as cooling water
Municipal	119 (0.0315)	455 (109)	

Water Usage:

Type	cu m/day (mgd)	l/kkg (gal/ton)	Recycled
Cooling	1,430 (0.378)	5,430 (1,300)	None
Process	119 (0.0315)	455 (109)	variable

Treatments are carried out for the two emerging waste streams. These streams are fed to settling ponds to remove suspended solids and then discharged.

Stream	Source	l/kkg (gal/ton)	Treatment	Disposal
Settling Pond Overflow	Slurry thickener	287 (69)	Settling Pond	Plant Effluent
Cooling Water (Discharge)	Various heat exchange devices found throughout plant	5,430 (1,300)	a) Containment of wastes b) Cooling water segregation c) Some water recycling d) Collection and sampling of wastes	Effluent

Individual effluents from this plant are combined with other sewer effluents. Some wastes are treated in conjunction with soda ash plant wastes. Tabulated loads are based on reasonable allocations.

The effluent from plant 166 contains 20,000 mg/l of dissolved solids (mostly dissolved carbonates), amounting to 5.75 kg/kkg of product (11.5 lb/ton). All of the bicarbonate wastes are treated along with chlor-alkali and soda ash wastes at the 166 facility in a common treatment system prior to discharge. There are no net effluent loads to the cooling water based on average daily operation. There are no organics in the plant effluent.

Plant 166 has plans to use the weak slurry thickener overflow, which constitutes their present source of waste, as a source of liquid for the product dryer scrubber and to recycle this liquid (concentrated with respect to sodium carbonate) back to the process. These process changes will eliminate the discharge of process waste waters.

Verification measurements on the plant intake water, cooling water, and effluent are given in Table 18. The similarity of composition of plant intake and cooling water discharge verifies segregation of cooling water from process water. The process effluent measured is the effluent of the whole plant complex and hence is not indicative of that of an isolated bicarbonate unit.

Sodium Carbonate

Soda ash is produced by mining and by the Solvay Process. In the Solvay Process sodium chloride brine is purified to remove calcium and magnesium compounds. It is reacted with ammonia and carbon dioxide produced from limestone calcination to yield crude sodium bicarbonate which is recovered from the solutions by filtration. The bicarbonate is calcined to yield soda ash. The spent ammonia solution is reacted with slaked lime and distilled to recover ammonia values for process recycle. The calcium chloride formed as a by-product during the distillation is either discharged as a waste or recovered by evaporation. Figure 50 shows a process flowsheet for the facility at plant 166. Although all Solvay Process plants have high dissolved solids effluents, this plant is unusual in that it recovers a significant amount of an otherwise wasted by-product. Since the market for calcium chloride will not absorb the by-product generated from such recovery from all Solvay plants, this plant cannot be considered to be exemplary on this basis.

The raw waste loads for the 166 facility consist of brine purification muds, unreacted sodium chloride and the calcium chloride by-product, as follows:

TABLE 18. Plant 166 Verification Data

Parameter	Plant Intake		Bicarbonate Cooling Water	Plant Complex Effluent
	Measured	Furnished		
Flow, cu m/day (MGD)	Not measured	188,000 (49.5)*	Not Measured	17,400 (4.6)
Temperature, °C	11.2	-	Not Measured	Not Measured
Color (Apparent) APHA Units	20	-	270	275
Turbidity, FTU	10	27	30	0
Conductivity,				
mg/l NaCl	2000	-	1800	67,000
micromhos/cm	3800	-	3400	118,000
Suspended Solids, mg/l	5	-	160	206
Dissolved Solids, mg/l	2850	-	2560	76,000
pH	7.80	-	7.75	10.8
Acidity:				
Total, mg/l $CaCO_3$	0	-	0	0
Free, mg/l $CaCO_3$	0	-	0	0
Alkalinity (Total)				
P, mg/l $CaCO_3$	0	-	0	460
T, mg/l $CaCO_3$	195	171	305	610
Hardness:				
Total, mg/l $CaCO_3$	1300	1428	1000	45,000
Calcium, mg/l $CaCO_3$	1250	571	950	45,000
Halogens:				
Chlorine, mg/l	0.1	-	1.9	0
Chloride, mg/l	1525	-	1275	-
Fluoride, mg/l	0.45	-	0.50	1.36
Sulfate, mg/l	170	-	130	640
Phosphates				
Total, mg/l	1.1	-	1.0	0.7
Nitrogen				
Total, mg/l N	0.55	-	0.43	1.7
Heavy Metals: Iron mg/l Fe	0.07	-	0	0.48
Chromate, mg/l Cr^{+6}	0.01	-	0	0
Oxygen (Dissolved), mg/l O_2	4.7	-	13	4

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*Furnishes cooling water to whole plant

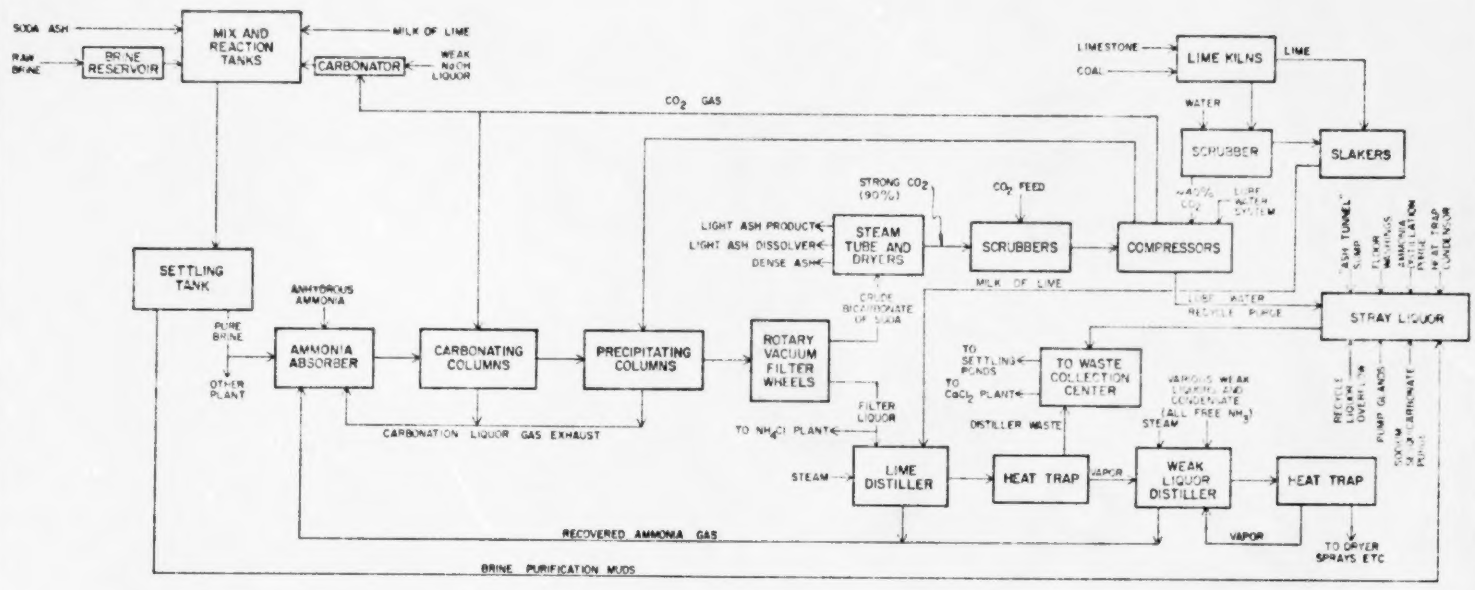
SODA ASH
RAW BRINE
BRINE RESERVOIR
MIX AND REACTION TANKS
MILK OF LIME
CARBONATOR
WEAK NaOH LIQUOR
CO2 GAS
LIMESTONE
COAL
LIME KILNS
LIME
WATER
SCRUBBER
SLAKERS
~40% CO2
LUBE WATER SYSTEM
STRONG CO2 (90%)
CO2 FEED
LIGHT ASH PRODUCT
LIGHT ASH DISSOLVER
DENSE ASH
STEAM TUBE AND DRYERS
SCRUBBERS
COMPRESSORS
"ASH TUNNEL" SUMP
FLOOR WASHINGS
AMMONIA DISTILLATION PURGE
HEAT TRAP CONDENSOR
SETTLING TANK
ANHYDROUS AMMONIA
PURE BRINE
OTHER PLANT
AMMONIA ABSORBER
CARBONATING COLUMNS
PRECIPITATING COLUMNS
ROTARY VACUUM FILTER WHEELS
CRUDE BICARBONATE OF SODA
MILK OF LIME
LUBE WATER RECYCLE PURGE
STRAY LIQUOR
TO SETTLING PONDS
TO CaCl2 PLANT
TO WASTE COLLECTION CENTER
VARIOUS WEAK LIQUORS AND CONDENSATE (ALL FREE NH3)
RECYCLE LIQUOR OVERFLOW
PUMP GLANDS
SODIUM SESQUICARBONATE PURGE
CARBONATION LIQUOR GAS EXHAUST
FILTER LIQUOR
TO NH4Cl PLANT
DISTILLER WASTE
STEAM
STEAM
LIME DISTILLER
HEAT TRAP
VAPOR
WEAK LIQUOR DISTILLER
HEAT TRAP
VAPOR
TO DRYER SPRAYS ETC
RECOVERED AMMONIA GAS
BRINE PURIFICATION MUDS

FIGURE 50
SOLVAY SODA ASH PROCESS FLOW DIAGRAM AT PLANT 166

Waste Products	Process Source	kg/kkg of Soda Ash (lb/ton)
1. $CaCO_3$	DS, B, P	84.5 (169)
2. Na_2CO_3	B	0.3 (0.6)
3. $CaSO_3$	DS	31 (62)
4. NaCl	DS, B	510.5 (1021)
5. $CaCl_2$	DS	1090 (2180)
6. Na_2SO_4	B	0.8 (1.6)
7. $Fe(OH)_3$	B	0.1 (0.2)
8. $Mg(OH)_2$	DS, B, P	48.5 (97)
9. CaO (inactive)	DS, B	109.5 (219)
10. NaOH	B	0.05 (0.1)
11. SiO_2	DS, B	58.5 (117)
12. CaO (active)	DS	24 (48)
13. NH_3	DS	0.15 (0.3)
14. H_2S	DS	0.02 (0.04)
15. Ash & Cinders	P	40 (80)

DS = Distillation, B = Brine, P = Power

Water Inputs to Plant:

Type	l/kkg (gal/ton)	Comments
River	3,650 (875)	Sent to Power Section for boiler feed water
Lake	4,680 (1,120)	Treated prior to use with chlorine
Municipal	2,030 (486)	Majority is sent to Power Section for boiler feedwater

Water Flows:

Type	l/kkg (gal/ton)	Recycled
Cooling	52,100 (12,500)	
Process	4.5 (1.1)	0
Sanitary	Est. 74-149 (18-36)	0
Boiler Feed	5,420 (1,300)	0

The maximum process water use is about 149 l/kkg (36 gal/ton), but the average is only 4.5 l/kkg (1.1 gal/ton).

Most of the water use is for cooling purposes and little stream recycling is employed. Treatment methods in use are:

Stream	Source	Treatment	Disposal
Cooling water effluent	Various heat exchangers throughout plant	a. Internal recycle b. Segregation of waste c. Collection and containment of wastes	Disposal to cooling water sewer system
Settling pond effluent	Distiller wastes	Settling out suspended solids with coagulation and precipitation of metals and other chemicals	Discharge to source of cooling water

Individual effluents from this plant are combined with other effluents.

Treatment consists of use of settling ponds and some pH control prior to discharge. The performance of this treatment is detailed below:

Method	Qualitative Rating	Waste Reduction Accomplished
Evaporation of distiller waste	Good	Reduces CaCl by 21 percent NaCl by 4 percent
Settling Ponds	Excellent	Suspended solids reduced by 99 percent+

In addition, two other methods of treatment are used or planned:

(1) part of the wastes may be used for municipal waste treatment.
(2) part of the raw distiller waste stream is diverted to a small plant for calcium chloride recovery. About 21 percent of the calcium chloride in the raw waste is recovered on this sidestream.

The plant effluent after treatment contains about 100,000 mg/l dissolved solids (mostly NaCl and $CaCl_2$) in the process waste stream and is also fairly high in suspended solids. This type of effluent is typical of a Solvay process plant.

Calcium Chloride Recovery

The flow diagram for the calcium chloride recovery process at plant 166 is shown in Figure 51. The waste stream is first cycled through a number of partial evaporation and filtration steps to concentrate the waste solutions. After this, further partial evaporation is used to selectively remove the sodium chloride from solution and then total evaporation is used to recover calcium chloride from the remaining solution.

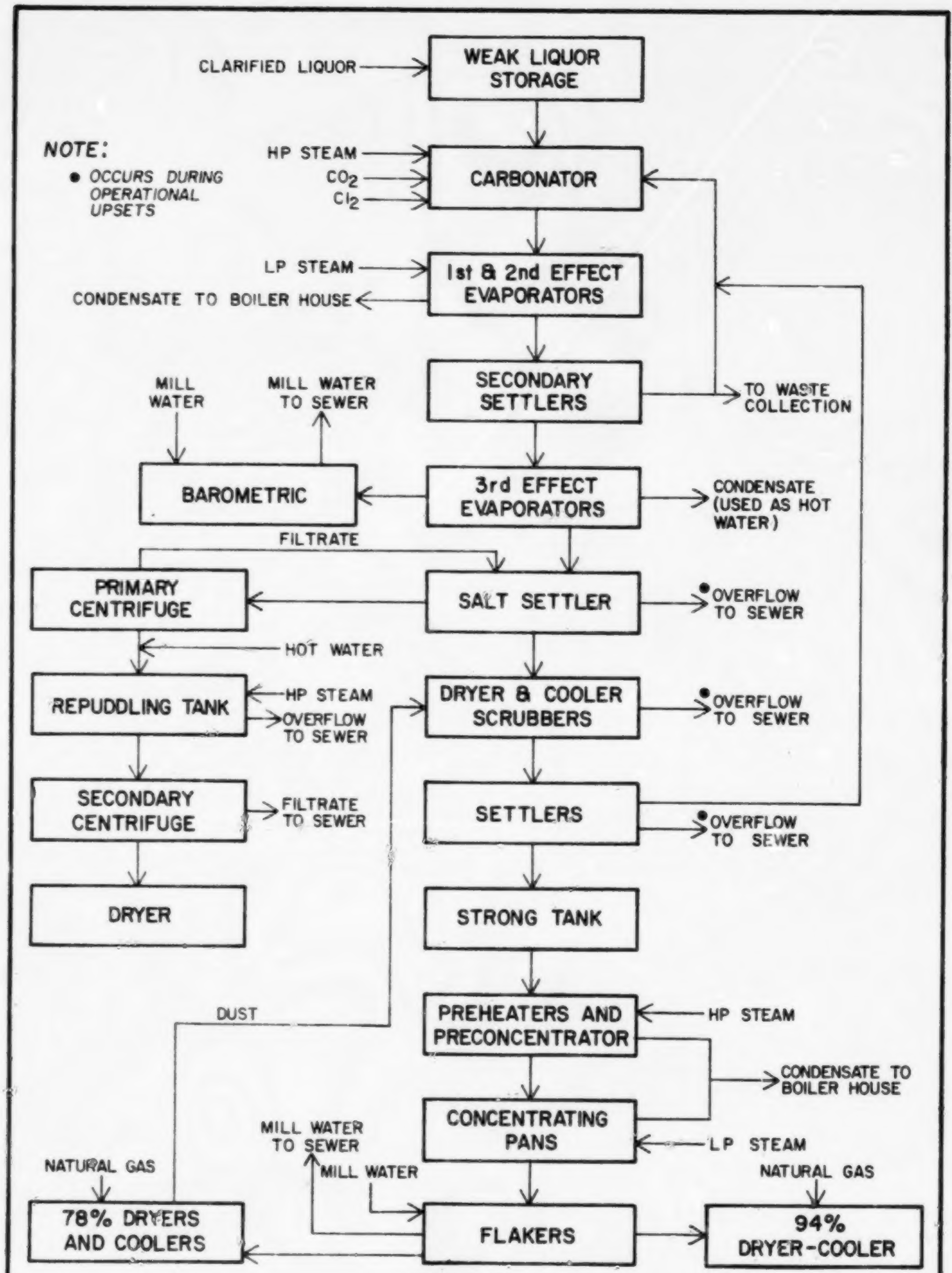
CLARIFIED LIQUOR
WEAK LIQUOR STORAGE
NOTE:
● OCCURS DURING OPERATIONAL UPSETS
HP STEAM
CO_2
Cl_2
CARBONATOR
LP STEAM
1st & 2nd EFFECT EVAPORATORS
CONDENSATE TO BOILER HOUSE
MILL WATER
MILL WATER TO SEWER
SECONDARY SETTLERS
TO WASTE COLLECTION
BAROMETRIC
3rd EFFECT EVAPORATORS
CONDENSATE (USED AS HOT WATER)
FILTRATE
PRIMARY CENTRIFUGE
SALT SETTLER
●OVERFLOW TO SEWER
HOT WATER
REPUDDLING TANK
HP STEAM
OVERFLOW TO SEWER
DRYER & COOLER SCRUBBERS
●OVERFLOW TO SEWER
SECONDARY CENTRIFUGE
FILTRATE TO SEWER
SETTLERS
●OVERFLOW TO SEWER
DRYER
STRONG TANK
DUST
PREHEATERS AND PRECONCENTRATOR
HP STEAM
CONDENSATE TO BOILER HOUSE
CONCENTRATING PANS
LP STEAM
MILL WATER TO SEWER
MILL WATER
NATURAL GAS
78% DRYERS AND COOLERS
FLAKERS
NATURAL GAS
94% DRYER-COOLER

FIGURE 51
CALCIUM CHLORIDE RECOVERY PROCESS
AT PLANT 166

Table 19 shows the raw wastes produced in this recovery operation and some other data. The principal waste is a contaminated sodium chloride co-product which is discarded, as well as some calcium chloride from condensates and spills. Water use for this recovery process is:

A. Water Inputs to Plant

Type	l/kkg of 100 percent $CaCl_2$ (gal/ton)	Comments
River	3,910 (938)	Steam generation
Lake	118,500 (28,400)	Cooling
Municipal	434 (104)	Steam generation

B. Water Usage

Type	l/kkg of 100 percent $CaCl_2$ (gal/ton)
Cooling	118,500 (28,400)
Process	3,850 (923)

The present recovery unit reduces the effluent calcium chloride by about 21 percent. This is because of the limited market for calcium chloride. According to the manufacturer, if more of the material could be marketed, more would be recovered. An evaporation process for its recovery, as can be seen from this discussion, is already operative. This recovery step, as it is now practiced, also reduces the sodium chloride effluent of the Solvay process by 4 percent.

Table 20 shows verification measurements on the water intake, the calcium chloride cooling water, the final effluent and the soda ash cooling water.

Sodium chloride

Sodium chloride is produced by three methods:

1) Solar evaporation of seawater;
2) Solution mining of natural brines;
3) Conventional mining of rock salt.

a) Solar evaporation process

In the solar evaporation process, sea water is concentrated by evaporation in open ponds to yield a saturated brine solution. After saturation is reached, the brine is then fed to a crystallizer, wherein sodium chloride precipitates, leaving

TABLE 19. Calcium Chloride Recovery Process

A. Raw Materials for Product

1. Soda ash distiller waste
2. Chlorine
3. Carbon dioxide 40% CO_2
4. Captive steam and power

B. Raw Waste Loads

Waste Products	Process Source	kg/kkg (lb/ton) of Product*
1. Ash and cinders	Steam and power	42.5(85)
2. Water purification sludge	Steam	0.75(1.5)
3. NaCl co-product	Evaporation	235(470)
4. $CaCl_2$	Condensates and spills	35-50(70-100)

C. Comments

Ratio of $CaCl_2$ to NaCl available in distiller waste is approximately 1.4. Market demand at this location is at a ratio of 10.6 to 1.

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*Product is 100% calcium chloride.

TABLE 20. Verification Measurements at Plant 166

Parameter*		Water Intake	CaCl2 Cooling Water	Final Effluent	Soda Ash Cooling Water
Flow, cu m/day		Not Measured	Not Measured	17,400	Not Measured
Temperature, °C		11.2	23.8	-	"
Color (Apparent) APHA Units		20	35	275	110
Turbidity, FTU		10	15	0	5
Conductivity,		2000 (NaCl);	4000	67,000	21,000
micromhos/cm		3800	7500	118,000	4,400
Suspended Solids		5	10	170	30
pH		7.80	7.95	10.8	7.8
Acidity: Total		0 CaCO3	0	0	0
Free		0 "	0	0	0
Alkalinity (Total)	P	0 "	0	460	0
	T	195 "	190	610	240
Hardness: Total		1300"	1400	45,000	1,270
Calcium		1250"	1350	45,000	1,120
Halogens: Chlorine		0.1	0.6	0	1.7
Chloride		1525	2600	50,000	1,350
Fluoride		0.45	0.55	1.36	0.6
Sulfate		170	170	640	190
Phosphates (Total)		1.1	1.2	0.7	1.6
Nitrogen (Total)		0.55	0.58	1.7	0.48
Heavy Metals: Iron		0.07	0.18	0.48	0.12
Chromate		0.01	0	0	0
Oxygen (Dissolved)		4.7	7.7	4	10
COD		175	-	-	-

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*mg/1 unless otherwise specified.

behind a concentrated brine solution (bittern) consisting of sodium, potassium and magnesium salts. The precipitated sodium chloride is recovered for sale and the brine is then further evaporated to recover additional sodium chloride values and is then either stored, discharged back to salt water or further worked to recover potassium and magnesium salts.

In the solar evaporation process, all of the wastes are present in the bittern solution. Typical bittern analysis for the exemplary 059 facility is given in Table 21. No bittern is discharged from this facility. The bittern is stored and, in the past, has been worked for recovery of other materials.

At plant 059, treatment consists of storage and further use of the bittern materials. The plant water usage is:

Type	Use	Source	cu m/day (mgd)	l/kkg (gal/ton)	Recycle
Process	Refining process	Well	2,270 (0.60)	894 (214)	100 percent
Process	Raw Material	Bay	327,000 (86.4)	129,000 (30,900)	None

As the bitterns are stored and further worked, there is no discharge. Eventual total evaporation after further bittern use yields only solid wastes. Sufficient land and ponding area is available at the 059 facility to store bitterns for the next 30-50 years.

b) Solution brine-mining process

Saturated brine for the production of evaporated salt is usually obtained by pumping water into an underground salt deposit and removing the saturated salt solution from an adjacent interconnected well, or from the same well by means of an annular pipe. Besides sodium chloride, the brine will contain some calcium sulfate, calcium chloride, magnesium chloride, and lesser amounts of other materials including iron salts and sulfides.

The chemical treatment given to brines varies from plant to plant depending on the impurities present. Typically, the brine is first aerated to remove hydrogen sulfide and, in many cases, small amounts of chlorine are added to complete sulfide removal and oxidize all iron salts present to the ferric state. The brine is then pumped to settling tanks where it is treated with soda ash and caustic soda to remove most of the calcium, magnesium and iron present as insoluble salts. After clarification to remove these insolubles, the brine is sent to multiple-effect evaporators. As water is removed, salt crystals form and are removed as a slurry. After screening to remove lumps, the slurry is washed with fresh brine to remove fine

TABLE 21. Chemical Analysis of Bittern

Parameter*	
pH	7.8
Total Solids	241550
Total Volative Solids	86600
Total Suspended Solids	1760
Total Dissolved Solids	239790
Alkalinity as $CaCO_3$	2800
BOD	198
COD	6350
Ammonia as N	0.702
Kjeldahl Nitrogen Total	32.610
Nitrate as N	37.50
Phosphorus Total as P	0.22
Chloride	158000
Cyanide	0.04
Fluoride	74.90
Phenols	0.064
Sulfate as S	21000
Sulfide as S	2
TOC	900
Aluminum	2.5
Arsenic	0.04
Cadmium	0.02
Calcium	450
Chromium	0.02
Iron	6.5
Mercury	0.001
Sodium	5500
Titanium	0.02
Zinc	0.19

* All units mg/l unless otherwise specified.

crystals of calcium sulfate from the mother liquor to the slurry. These solids are returned to the evaporator. The calcium sulfate concentration in the evaporator eventually builds up to the point where it must be removed by "boiling out" the evaporators.

The washed slurry is filtered, the mother liquor is returned to the evaporators, and the salt crystals from the filter are dried and screened. Salt thus produced from a typical brine will be of 99.8 percent purity or greater. Some plants do not treat the raw brine, but control the calcium and magnesium impurities by watching the concentrations in the evaporators and bleeding off sufficient brine to maintain predetermined levels. By such methods, salt of better than 99.5 percent purity can be made. In either case, the final screening of the dried salt yields various grades depending on particle size. The facility at plant 030 is similar to the standard flow diagram shown in Section IV.

A detailed list of the raw wastes and their process sources is shown below. These include wastes from the multiple evaporators and dryers, sludges from basic purification, as well as water treatment chemicals used for the cooling water:

Waste Products	Process Source	Avg. kg/kkg of Product (lb/ton)	
NaOH	Boiler Blowdown	0.0055	(0.011)
Na_3PO_4	" "	0.0015	(0.003)
Na_2SiO_3	" "	0.0025	(0.005)
Na_2SO_3	" "	0.0015	(0.003)
NaCl & $CaSO_4$	Purge from multiple evaporator	0.045	(0.090)
NaCl	Evaporator	0.04	(0.08)
NaCl	Barometric condenser	1.1	(2.2)
NaCl	Miscellaneous sources	-	
Brine sludges	Brine purification	91 kkg/year (100 ton/year)	

The brine sludges are returned to the brine wells for settling and disposal.

Well water for brine field use is taken into the plant at a rate of 2,240 l/kkg of product (536 gal/ton). Lake water for cooling and other uses is drawn into the plant at a rate of 48,000 l/kkg (11,400 gal/ton).

Use	Flow	Recycle
Cooling (barometric condensers)	41,700 l/kkg (10,000 gal/ton)	none
Other (dust collection pumps)	6,400 l/kkg (1,540 gal/ton)	90 percent

Treatments of the effluent streams are as follows:

Stream No.	Source	Treatment
1	Condenser Discharge	To Lake
2	Storm Drain	To Lake
3	Tunnel Line (Lake Water)	To Lake
4	Ash Lime Discharge	Recycled

The storm drain flow cited above was 3,790 l/kkg of product (910 gal/ton) on the average.

The plant effluent streams #1 and #2 after treatment consist solely of streams containing 100 mg/l chloride at a pH of 8.2. Chloride concentration at the plant intake was given as 70-80 mg/l, with a pH of 8.2. Table 22 shows verification measurements on the plant intake and condenser discharge (stream #1) effluent. The chloride content and pH as stated are verified within a reasonable margin.

Sodium Dichromate and Sodium Sulfate

Sodium dichromate is prepared by calcining a mixture of chrome ore (FeO.Cr2O3), soda ash and lime, followed by water leaching and acidification of the soluble chromates. The insoluble residue from the leaching operation is recycled to leach out additional material.

During the first acidification step, the pH of the chromate solution is adjusted to precipitate calcium salts. Further acidification converts it to the dichromate and a subsequent evaporation step crystallizes sodium sulfate (salt cake) out of the liquor. The sulfate is then dried and sold. The solutions remaining after sulfate removal are further evaporated to recover sodium dichromate. Chromic acid is produced from sodium dichromate by reaction with sulfuric acid. Sodium bisulfate is a by-product. Figure 52 shows a detailed flowsheet for the exemplary facility at plant 184.

Plant 184 manufactures only sodium dichromate and chromic acid. However, some other chromate plants do convert part of their chromic acid products to potassium dichromate. All of this latter material is made in plants that produce other chromates.

The raw waste loads expected from the manufacture of sodium dichromate and its by-product sodium sulfate are given below. The bulk of the waste originates from the undigested portions of the ores used. These materials are mostly solid wastes. The wastes arising from spills and washdowns contain most of the hexavalent chromium. The wastes from water treatment and boiler

TABLE 22. Verification Measurements at Plant 030

Parameter*		Intake	Condenser Discharge
Flow, cu m/day (MGD)		37,900(10)	37,900(10.0)
Temperature, °C		13	22.5-23.0
Color, APHA Std.		40	40
Turbidity(FTU)		10	15
Conductivity(NaCl)		225	320
Suspended Solids		0	0
pH		8.0	8.1
Acidity: Total		0	0
Free		0	0
Alkalinity (Total)	P	0	0
	T	139	140
Hardness: Total		171	189
Calcium		128	147
Halogens: Chloride		65	120
Sulfate		13	37
Phosphates		0.07	0.1
Nitrogen		0.17	0.17
Heavy Metals: Iron		0.24	0.23
Oxygen (Dissolved)		-	2.8
COD		55	50

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*mg/l unless otherwise specified.

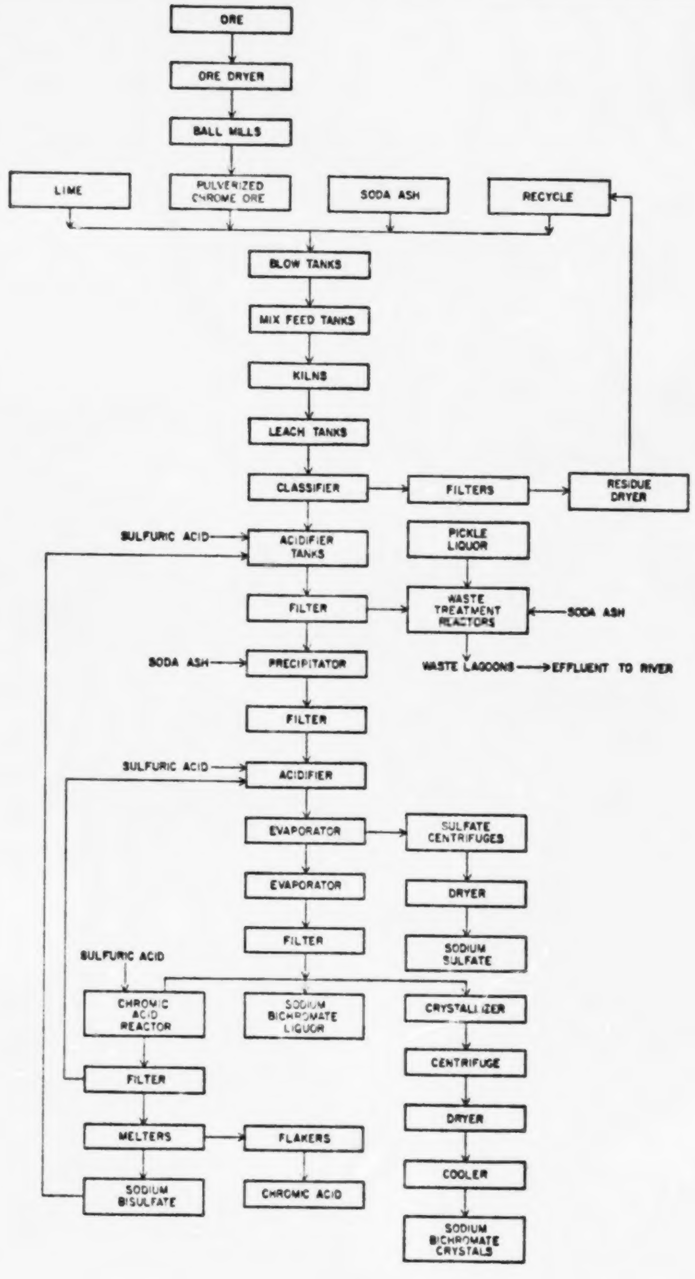
ORE
ORE DRYER
BALL MILLS
LIME
PULVERIZED CHROME ORE
SODA ASH
RECYCLE
BLOW TANKS
MIX FEED TANKS
KILNS
LEACH TANKS
CLASSIFIER
FILTERS
RESIDUE DRYER
SULFURIC ACID
ACIDIFIER TANKS
PICKLE LIQUOR
FILTER
WASTE TREATMENT REACTORS
SODA ASH
SODA ASH
PRECIPITATOR
WASTE LAGOONS
EFFLUENT TO RIVER
FILTER
SULFURIC ACID
ACIDIFIER
EVAPORATOR
SULFATE CENTRIFUGES
EVAPORATOR
DRYER
FILTER
SODIUM SULFATE
SULFURIC ACID
CHROMIC ACID REACTOR
SODIUM BICHROMATE LIQUOR
CRYSTALLIZER
FILTER
CENTRIFUGE
MELTERS
FLAKERS
DRYER
SODIUM BISULFATE
CHROMIC ACID
COOLER
SODIUM BICHROMATE CRYSTALS

FIGURE 52
CHROMATE MANUFACTURING FACILITY
AT PLANT 184

blowdowns are principally dissolved sulfates and chlorides. The manufacture of chromic acid contributes no additional wastes.

Waste Product	Process Source	kg/kkg of $Na_2Cr_2O_7$ Product (lb/ton) Average	Range
1. Chromate wastes (Materials not digested in H_2SO_4)	Residues	900(1800)	-
2. Washdowns* spills, etc.	--	0.75(1.5)	0.5-1(1-2)
3. Blowdown	Boilers and cooling towers	--	0.5-1(1-2)

---

*Includes contributions from the chromic acid unit.

Water intake to this facility consists of river water and well water in the following amounts based on sodium dichromate product: 12,700 l/kkg (3,030 gal/ton) and 1,840 l/kkg (440 gal/ton) respectively. The boiler feed comes from the river water feed and is softened prior to use. The well water is all filtered, softened and chlorinated.

Water Use:

Type	l/kkg of sodium dichromate (gal/ton)	Percent Recycled
Cooling	275,000 (66,000)	98.2
Products and Evaporation	5,400 (1,300)	0
Waste Treatment	8,860 (2,120)	0
Sanitary	255 (60)	0

Waste waters are treated with pickle liquor to effect reduction of chromates present. All effluent waters are lagooned to settle out suspended solids. This treatment removes 99 percent of the hexavalent chromium and the discharge contains 0.01 mg/l. The lagoon discharges to a nearby river when full.

All rainwater, washdowns, spills and minor leaks in the part of the plant which handles hexavalent chromium are captured in the area's sumps and used in the process. Storage facilities are provided to contain a heavy rain and return the water either to the process or to treatment. Separate rainwater drainage is provided for areas not handling hexavalent chromium. Sewers are continuously monitored. A batch system is used in the treatment process. Each batch is treated and analyzed before release to the lagoon.

Data on the effluent from this exemplary chromate treatment facility are presented below:

	Average	Range
Flow, liters/kkg (gal/ton)	8,860 (2,120)	-
Total Suspended Solids, mg/l	14	1-24
Total Dissolved Solids, mg/l	10,000	5,000 - 13,000 (mostly chlorides)
pH	7.2	6.0 - 8.5
Cr+3, mg/l	0.14 (mostly in form of suspended solids)	0.01 - 0.31
Cr+6, mg/l	0.01	

The chromium content has been significantly reduced. However, the amount of sodium chloride being discharged is significant. Based on the porous nature of the present lagoon walls and the high dissolved solids content discharged into the river, this plant is considered exemplary only from the standpoint of chromate control and treatment.

Table 23 gives a more detailed presentation for the river intake and plant effluent from this facility. The composition of river water taken near the plant and the plant effluent determined on two separate occasions are shown as a range of values. These data were furnished by the plant.

Tables 24 and 25 present data obtained by sampling for this facility. Table 24 shows an analysis of river water drawn adjacent to the plant. Table 25 shows the compositions of waste stream before and after passage through the pickle liquor treatment unit.

Sodium Metal

Sodium is manufactured by electrolysis of molten sodium chloride in a Downs electrolytic cell. After salt purification to remove calcium and magnesium salts and sulfates, the sodium chloride is dried and fed to the cell, where calcium chloride is added to give a low-melting $CaCl_2$-NaCl eutectic, which is then electrolyzed. Sodium is formed at one electrode, collected as a liquid, filtered and sold. The chlorine liberated at the other electrode is first dried with sulfuric acid and then purified, compressed, liquified and sold. Figure 53 shows the process in use and waste treatment facilities at plant 096.

There is no waste during operation of an individual cell for the molten salt electrolysis step in the Downs cell process. The cells are run in banks, and individual cells are cleaned out and refilled after the electrolyte is depleted. All of the wastes arise from this cleaning and refilling of individual cells.

TABLE 23. Intake and Effluent Composition at Plant 184

Parameter	River Water	Plant Effluent
Total Solids	79	330-334
Organic Solids	45	93-104
Mineral Solids	34	230-232
Alkalinity as $CaCO_3$ (methyl-orange)	2.0	0.0
Alkalinity (phenolphthalein)	0.0	0.0
Free Carbon Dioxide	1.6	1.0-17.0
Total Hardness (as $CaCO_3$)	15	209.3-238.7
Total Hardness (grains per gallon)	0.88	12.2-12.8
pH	6.4	7.4-8.4
Analysis of Mineral Solids:		
Silica (SiO_2)	2.6	5.0-6.0
Iron Oxide (Fe_2O_3)	0.4	0.1-0.3
Alumina (Al_2O_3)	0.8	0.0
Lime (CaO)	5.6	114.4-115.5
Magnesia (MgO)	2.0	0.8-5.0
Sulphate (SO_3)	6.8	3.4
Chloride (Cl)	8.9	1.3-1.8
Soda (Na_2O)	5.7	8.2-10.4
Manganese (Mn)	0.0	0.0
Fluoride (F)	0.0	0.0
Biochemical Oxygen Demand (BOD_5)	less than 5	-
Color (Pt-Co)	130	
Chromium (Cr)	-	**
Tannin	2.6	**

---

*mg/l unless otherwise specified

**None found

TABLE 24. Analysis of River Water at Plant 184

Parameter	Measurements (mg/l unless otherwise specified
Color, APHA Units	270
Turbidity, FTU	5
Conductivity	35 NaCl eq.
Suspended Solids	5
pH	6.59
Alkalinity (Total)	phen-0/Total-20 (as $CaCO_3$)
Hardness: (Total)	23 (as $CaCO_3$)
(Calcium)	15
Halogens: Chloride	11
Sulfate	0
Phosphate	0.38
Nitrate	0.13 (as N)
Heavy Metals: Iron	1.5
Chromium (Cr^{+6})	0*

---

*less than 20 mcg/l

TABLE 25. Analysis of Waste Treatment Streams at Plant 184

Parameter	Before Treatment	After Treatment
Flow	Batch volume - 28,700 liters	Batch volume - 30,400 liters
Temperature, °C	49	61
Color	500 (supernatant liquid)	70
Conductivity	5000 NaCl	14,500
Dissolved Solids	10,700	18,000
Suspended Solids	170,000	154,000
pH	10 (straight); 9.3 (dilution)	9.1 (supernatant, fresh); 8.4 (filtered, 30 days old)
Alkalinity (Total)	phen-0/total-1000 (as $CaCO_3$)	phen-2/total-23 (as $CaCO_3$)
Hardness: Total	600 (as $CaCO_3$)	6,000
Calcium	520 (as $CaCO_3$)	6,000
Halogens: Chloride	310	8,700
Sulfate	3,900	1,900
Phosphate	0.7	0.7
Nitrate	9.8 (as N)	-
Heavy Metals:		
Chromium (Cr^{+6})	1,300	0.01
Iron	-	0.60
Oxygen (Dissolved)	10.4	-

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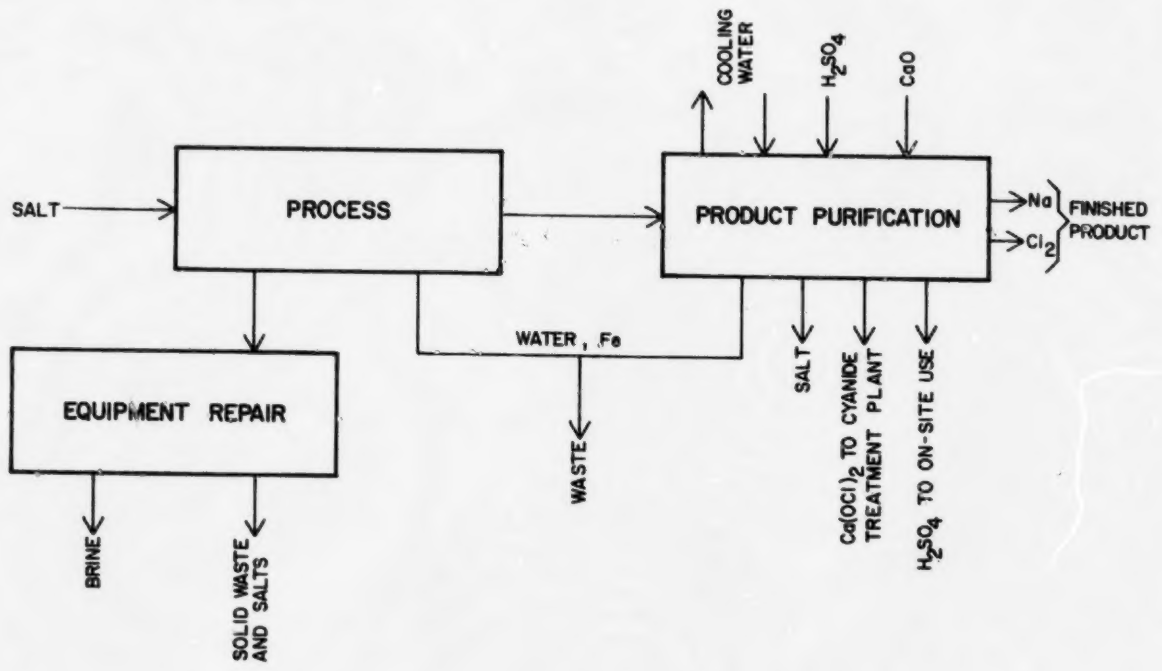
*mg/l unless otherwise specified.



SALT
PROCESS
PRODUCT PURIFICATION
COOLING WATER
H_2SO_4
CaO
Na
Cl_2
FINISHED PRODUCT
SALT
$Ca(OCl)_2$ TO CYANIDE TREATMENT PLANT
H_2SO_4 TO ON-SITE USE
WATER, Fe
WASTE
EQUIPMENT REPAIR
BRINE
SOLID WASTE AND SALTS

FIGURE 53
WASTE TREATMENT ON DOWNS CELL AT PLANT 096

The wastes produced by sodium manufacture at plant 096 are shown below. Several of the expected wastes are not present. This is due to the reuse of materials in other parts of the facility to make other products. For example, the sulfuric acid used in drying the chlorine is reused.

Waste Products	Process Source	kg/kkg of Product (lb/ton)
NaCl	Process	50-65 (100-130)
Misc. Alkaline Salts	Process	25-35 (50-70)
$Ca(OCl)_2$	Chlorine Recovery	45-75 (90-150)
Fe	Cooling Tower	0.065-0.095 (0.13-0.19)

The process does not normally shut down. The discharges result from the replacement of cells.

Cooling tower blowdowns and residual chlorine from tail gas scrubbers are discharged without treatment. The stream containing calcium hypochlorite wastes is used to treat cyanide wastes. Cooling water is discharged without treatment and tank wash and runoff water are first ponded to settle out suspended materials and then discharged.

The water input to the plant is well water in the amount of 2,730 cu m/day or 46,300 l/kkg of product (11,100 gal/ton), having an impurity content of:

Total Solids	110-125 mg/l
CO_2	30-60 mg/l
Hardness (as Ca)	80-100 mg/l
Fe	1-3 mg/l
Cu	0.02-0.06 mg/l
Zn	0.02 mg/l
Sulfate	2-7 mg/l
Alkalinity ($CaCO_3$)	70-100 mg/l

The water use within the plant is as follows:

Use	Flow	Amount
Cooling	29,100 cu m/day (7.7 mgd)	497,000 l/kkg (119,000 gal/ton)
Process	530 cu m/day (0.14 mgd)	9,000 l/kkg (2,150 gal/ton)

Table 26 lists the various plant waste streams and their compositions.

These stream effluents consist mostly of dissolved sodium chloride and other chlorides. Table 27 shows the results of analyses of simultaneous samples from three of the waste streams (those

TABLE 26. Plant 096 Effluent

Parameter*	Stream No. 1**	Stream No. 2***	Stream No. 3****	Stream No. 4*****
Flow, cu m/day (MGD)	409(0.108)	133(0.035)	1,780(0.470)	409(0.108)
TSS	30-50	50-70	5-10	-
TDS	400-600	-	300-400	-
BOD	-	-	-	-
COD	-	-	-	-
pH	6.5-7.5	10.5-12.0	6.7-7.5	-
Fe	2	1-2	2-3	-
Chloride	100-150	10,000-30,000	50-100	13,000
Chlorine	-	4,000-6,000	20-100	-
Sulfate	-	-	25-50	-
Total Hardness	-	-	180-225	-
Phosphate	0.2	-	-	-
Turbidity(FTU)	25-30	40-60	125	-
Color(APHA)	15	15	15	-
Acidity(Free)	20-30	20-30	-	-
Alkalinity (Total)	-	4,000-6,000	-	-
Hardness(Ca)	-	25,000-30,000	-	-

*All units mg/l unless otherwise specified.

**Cooling Tower Blowdown, Cl_2 Residual.

***Calcium hypochlorite used to treat cyanide wastes in another process.

****Cooling water.

*****Runoff, excess calcium hypochlorite, tank washup.

Note: There is also 2,270 liters/day (600 GPD) used sulfuric acid sent for use elsewhere in the complex and not discharged into surface streams.

TABLE 27. Plant 096 Effluent

Parameter*	Stream No. 2	Stream No. 3	Stream No. 4
Flow, cu m/day (MGD)			
Plant	-	-	-
VM**	133(0.035)	1,590(0.42)	-
Temperature, °C			
Plant	-	-	-
VM	21.5	22	20
Color(True), APHA Units			
Plant	15	15	15
VM	300	30	260
Turbidity, Jackson Units			
Plant	26	25	58
VM	82	10	45
Suspended Solids			
Plant	39	6	137
VM	39	11	90
Dissolved Solids			
Plant	574	355	-
VM	479	266	35,800
pH			
Plant	6.5	6.45	11.9
VM	6.55	6.44	11.9
Acidity(Free)			
Plant	19.5	37.5	-
VM	-	-	-
Alkalinity($CaCO_3$)			
Plant	-	-	-
VM	48	57	4,500
Chlorine			
Plant	0	0.6	64,000
VM	0	0.2	2,400
Chloride			
Plant	121	92	17,800
VM	125	90	26,500
Sulfate			
Plant	-	26	-
VM	-	10	-
Fe			
Plant	0.33	0.69	0.92
VM	0.22	2.7	0.7

---

*mg/l unless otherwise specified.

**Verification measurement

corresponding to streams 2, 3, and 4 of Table 26). Good agreement between the results was generally obtained.

This facility has good pH and suspended solids control and reuse of some wastes, but there are large amounts of chlorides being discharged which may be recycled for process reuse.

Sodium Silicate

Sodium silicate is manufactured by the reaction of soda ash or anhydrous sodium hydroxide with silica in a furnace, followed by dissolution of the product in water under pressure to prepare sodium silicate solutions. In some plants, the liquid silicate solutions are then further reacted with sodium hydroxide to manufacture metasilicates which are then isolated by evaporation and sold. Figure 54 shows the total system diagram for plant 072.

The raw waste loads for plant 072 are listed below. These wastes consist mostly of sodium silicate and unreacted silica:

Waste Products	Process Source	Avg. kg/kkg of Dry Basis Product (lb/ton)
Sodium Silicate	Scrubbers	37 (74)
Silica	Scrubbers	2.85 (5.7)
NaOH/Silicates	Washdowns	0.39 (0.78)

Data on in-plant water use could not be obtained from plant 072. However, the water use data from another plant (134) is given below on the basis of unit weight of product (dry basis). The water intake is 2,900 l/kkg (710 gal/ton) which is used as follows:

Water Use	l/kkg (gal/ton)
Process water	1,020 (245)
Boiler blow-down, Compressor cooling, Wash-down, Tank cleaning, and misc.	610 (147)
Steam, Evaporation, and other losses	1,330 (319)

At plant 072 all scrubber and washdown waters are sent to a totally enclosed evaporation pond. There is no plant effluent.

Sodium Sulfite

Sodium sulfite is manufactured by reaction of sulfur dioxide with soda ash. The crude sulfite formed in this reaction is then purified, filtered to remove insolubles from the purification

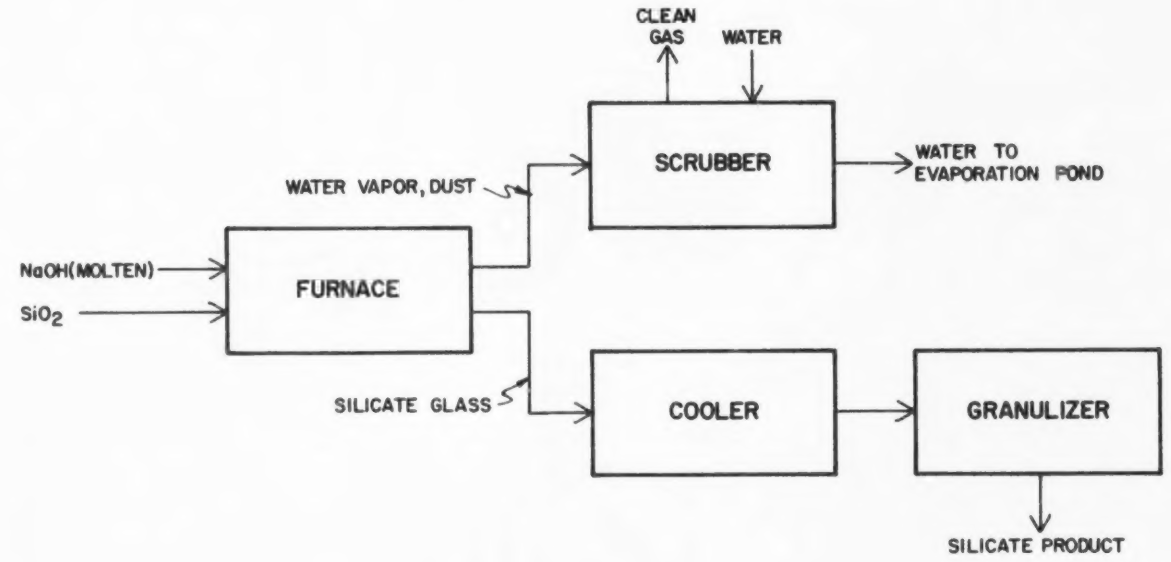

CLEAN GAS
WATER
WATER VAPOR, DUST
SCRUBBER
WATER TO EVAPORATION POND
NaOH(MOLTEN)
SiO_2
FURNACE
SILICATE GLASS
COOLER
GRANULIZER
SILICATE PRODUCT

FIGURE 54
SODIUM SILICATE MANUFACTURE AT PLANT 072

step, crystallized, dried and shipped. A process diagram for plant 168 is given in Figure 55.

A listing of the raw wastes produced from sodium sulfite production is given below. These consist of sulfides from the purification step and a solution produced by periodic vessel cleanouts containing sulfite and sulfate.

Waste Products	Process Source	kg/kkg of Product (lb/ton) Average	Range
Metal sulfides	Filter wash	0.755 (1.51)	0.19-1.44 (0.38-2.88)
Na_2SO_3/Na_2SO_4 solution	Dryer ejector	-	-
Na_2SO_3/Na_2SO_4 solution	Process cleanout	-	-

Cleanouts of various process vessels produce shock loads up to 9.1 kkg (10 tons) of sodium sulfite and sulfate (dry basis). Cleanouts are conducted 3-6 times per year. For this, separate tanks are used for surge capacity with bleed into the treatment unit over a 5-10 day period.

Approximately 244 cu m/kkg of product (57,600 gal/ton) of river water and 290 to 630 l/kkg (70 to 150 gal/ton) of municipal water are taken into the plant. The stated analysis and verification of the river intake is:

	Stated Concentration (mg/l)		
Parameter	Average	Range	Verification Measurement (mg/l)
pH	(6.80)	5.68-7.12	7.00
Suspended Solids	28	10-45	10
BOD	14.8	1.4-38.5	-
Iron	2.6	1.5-4.9	0.9
Copper	0.02	0.01-0.02	-
Chromium	0.01	0.01-0.02	-
Zinc	0.49	0.08-1.84	-
Nickel	0.01	0.01-0.02	-
Lead	0.02	0.01-0.07	0.1
Dissolved Solids	-	-	168

The in-plant use of the water intake is as follows:

Use	l/kkg (gal/ton)	Percent Recycle
Indirect cooling	Approx. 244,000 (57,600)	0
Process (condensate)	Approx. 170 (40)	0
Dryer, Ejector Filter Wash	290 to 630 (70 to 150)	0

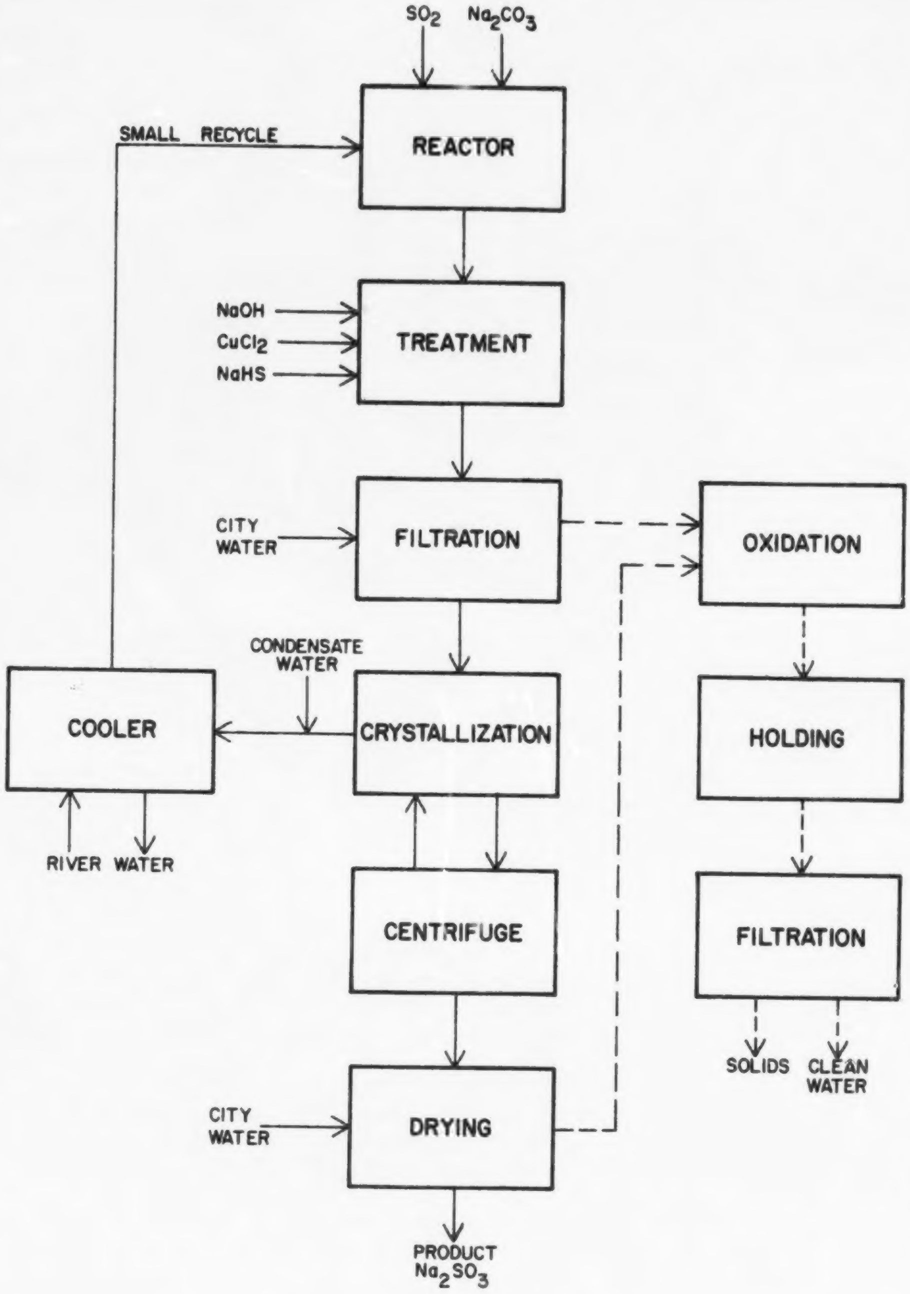

SO2
Na2CO3
SMALL RECYCLE
REACTOR
NaOH
CuCl2
NaHS
TREATMENT
CITY WATER
FILTRATION
OXIDATION
CONDENSATE WATER
COOLER
CRYSTALLIZATION
HOLDING
RIVER WATER
CENTRIFUGE
FILTRATION
SOLIDS
CLEAN WATER
CITY WATER
DRYING
PRODUCT Na2SO3

FIGURE 55
SODIUM SULFITE PROCESS FLOW DIAGRAM
AT PLANT 168

The principal waste streams operating on a continuous basis consist of flows from the dryer ejector and filter washing operations. These waters are treated by aeration and filtration prior to discharge. Vessel washouts are also subjected to the aeration and filtration procedure. The performance experience of oxidation and filtration treatment processes at this plant is:

Method	Qualitative Rating	Waste Reduction Accomplished
Oxidation	Excellent	94 percent oxidation of sulfite to sulfate
Filtration	Excellent	98 percent suspended solids removal

Compositions of the process effluents streams after treatments are given below. The waste stream after aeration treatment and after it has been subjected to a final filtration prior to discharge are shown. The cooling stream, which consists of untreated river water, has the same composition as measured at the intake. Measurements for verification of the process effluents and cooling water are given in Tables 28 and 29, respectively.

Parameter	After Aeration		After Final Filtration	
	Ave.	Range	Ave.	Range
TSS (mg/l)	2,200	700-4,100	97	3-240
TDS (mg/l)	57,000	46,000-70,000	57,000	46,000-70,000
BOD5	56.8 mg/l	46-71 mg/l	56.8 mg/l	46-71 mg/l
COD	118 mg/l	64-161 mg/l	118 mg/l	64-161 mg/l
pH	9.8	9.7-9.9	9.8	9.7-9.9
Temperature	65°C	-	43°C	38-49°C

Sulfuric Acid

Sulfuric acid is manufactured primarily by the contact process which involves catalytic oxidation of sulfur dioxide to sulfur trioxide and reaction of the sulfur trioxide with water to yield sulfuric acid. Within the contact process, there are three types of plants.

(1) Double absorption - paired sulfur trioxide absorption towers and catalyst beds in series are used to maximize conversion of sulfur dioxide so that tail gas scrubbers are not required.

(2) Single absorption - single absorption towers and catalyst beds are used and tail gases frequently have to be scrubbed to remove sulfur oxides; and

TABLE 28. Measurements of Plant 168 Process Waste Streams Before and After Treatment

Parameter*		Before**	After
Flow		(Batch Process)	(Batch Process)
Temperature, °C(°F)		76.7(170)	76.7(170)
Color(Apparent) APHA Std.		500	500
Turbidity, FTU		500	380
Total Dissolved Solids		88,200	93,900
Total Suspended Solids		780	2,010
pH		11.0	11.2
Alkalinity (Total)	P	9,000	2,500
	T	24,000	4,800
Hydrogen Sulfide		0	0
Sulfite		60,000	170
COD		8,000	250

---

*mg/l unless otherwise specified.

**This sample was collected from the full oxidation tank just before the waste treatment process was begun. This was necessary because the waste lines to the tank are not accessible for sampling and the only outlet valve is on the tank itself.

TABLE 29. Plant 168 Cooling Water Measurements

Parameter*		Intake	Effluent
Temperature, °C		17	21
Color(Apparent) APHA Std.		95	65
Turbidity, FTU		25	15
Conductivity, as NaCl		130	120
Suspended Solids		10	8
pH		7.00	7.08
Acidity: Total		0	0
Free		0	0
Alkalinity (Total)	P	0	0
	T	40	40
Hardness: Total		73	76
Calcium		50	51
Halogens: Chlorine		24	24
Sulfate		53	55
Phosphates		0.72	0.66
Nitrate		0.33	0.32
Heavy Metals: Iron		0.86	0.78
Hydrogen Sulfide		0	0
Sodium Sulfite		3	4

---

*mg/l unless otherwise specified.

(3) Spent acid plants - these plants use spent sulfuric acid in place of, or in addition to, sulfur as a raw material. While the acid production parts of these plants are the same as those for single absorption, these plants are unique because of the spent acid pyrolysis units used to convert the waste sulfuric acid raw materials to a sulfur dioxide feed stream.

In this section, only the first two types of plants are considered.

Double Absorption

In the double absorption contact process, sulfur is burned to yield sulfur dioxide which is then passed through a catalytic converter with air to produce sulfur trioxide. The sulfur trioxide is then abosrbed in 95-97 percent sulfuric acid. The gases emerging from the absorber are fed to a second converter to oxidize the remaining sulfur dioxide to sulfur trioxide which is then absorbed in a second absorption tower. The tail gases are vented to the atmosphere. Figure 56 shows a detailed process flow sheet for plant 086.

At plant 086, only cooling water is discharged. In double absorption plants, the tail gases are sufficiently depleted to sulfur oxides that there is no need for gas scrubbers. Also, at this plant, use of extensive maintenance and leak prevention has been employed to prevent discharge of any product acid.

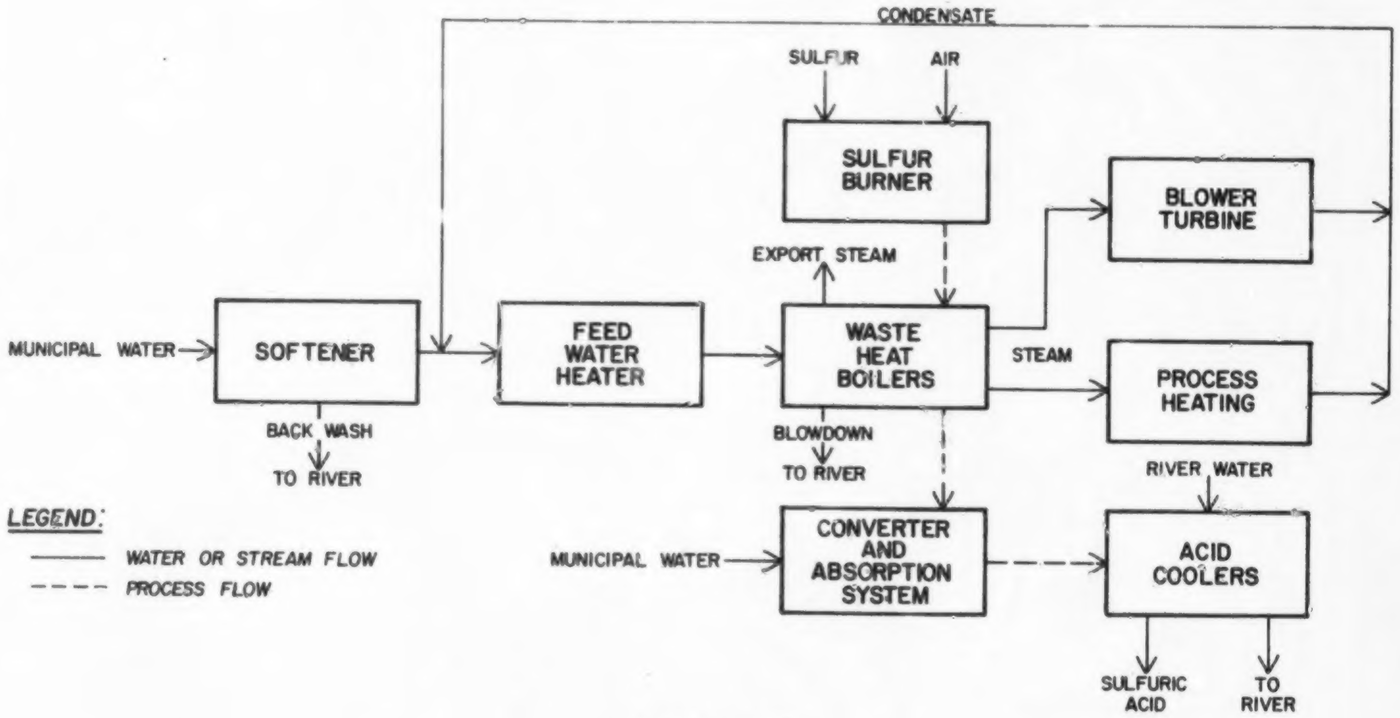
The table below shows water usage at plant 086. Most water is used for cooling. Process water is consumed to make sulfuric acid and is not discharged. The only plant effluent is the cooling water used in the heat exchangers and associated water treatment chemicals.

Water Inputs to Plant:

Type	cu m/day (mgd)	l/kkg (gal/ton)	Comments
River	35,200 (9.30)	55,600 (13,300)	Used for cooling only
Municipal	1,020 (0.27)	1,610 (386)	Used for process steam and cooling

Water Usage:

Type	Source	cu m/day(mgd)	l/kkg(gal/ton)	Percent Recycled
Cooling	River	35,200 (9.30)	55,600 (13,300)	0
	Municipal	295 (0.078)	463 (111)	0
Process	Municipal	117 (0.031)	184 (44)	0
Steam	Municipal	610 (0.161)	960 (230)	0



CONDENSATE
SULFUR
AIR
SULFUR BURNER
BLOWER TURBINE
EXPORT STEAM
MUNICIPAL WATER
SOFTENER
FEED WATER HEATER
WASTE HEAT BOILERS
STEAM
PROCESS HEATING
BACK WASH
TO RIVER
BLOWDOWN
TO RIVER
RIVER WATER
LEGEND:
WATER OR STREAM FLOW
PROCESS FLOW
MUNICIPAL WATER
CONVERTER AND ABSORPTION SYSTEM
ACID COOLERS
SULFURIC ACID
TO RIVER

FIGURE 56
DOUBLE ABSORPTION CONTACT SULFURIC ACID PROCESS
FLOW DIAGRAM AT PLANT 086

The only effluent from this facility is once-through cooling water. Table 30 shows verification measurements for the water intake and effluent.

Single Absorption

The single absorption process differs from that previously described only in the arrangement of converters and absorbers. The rest of the process is the same. For the single absorption process, the sulfur dioxide is passed through one or more converters and then into one or more absorbers prior to venting to the atmosphere. This arrangement is less effective for both conversion of sulfur dioxide to sulfur trioxide and for absorption of the sulfur trioxide into the absorber sulfuric acid. As a result, the tail gases may have to be scrubbed, creating a waterborne waste not present for double absorption plants. The exemplary plant is plant 141.

For the single absorption sulfur-burning process, there are no wastes from the sulfuric acid process itself. Wastes arise from the use of water treatment chemicals. The raw wastes are iron, silicon, calcium and magnesium salts from water treatment. This does not cover spent acid plants based on single absorption.

Most of the cooling water used at this plant is recycled and only 5 percent emerges from the plant. This is sent to evaporation ponds, from which there is no discharge. The water input is well water in the quantity of 606 cu m/day (0.160 mgd) or 1,670 l/kkg of product (400 gal/ton). This water is used as follows:

Type	cu m/day (mgd)	l/kkg (gal/ton)	Recycled
Cooling	560 (0.148)	1,540 (370)	95
Process	45.5 (0.012)	125 (30)	0

All waterborne wastes are sent to an evaporation pond. There is no discharge. Table 31 shows verification measurements on the intake water, the effluent going to the evaporation pond, and the evaporation pond water, respectively.

Titanium Dioxide

a) Chloride process

Virtually the same process is used at the two chloride process facilities studied (plants 009 and 160). The only process differences lie in the types of ore used. Plant 160 employs a unique process using an ore containing 66 percent titanium dioxide, while plant 009 uses only 95 percent plus grades of rutile and upgraded ilmenite. Figure 57 and 58 show the process flows within the 009 facility.

TABLE 30. Intake and Effluent Measurements at Plant 086

Parameter*	Intake	Effluent
Flow cu m/day (MGD)	Not Measured	11,350 (3.0)
Temperature, °C	13	26.5
Color (apparent - APHA std.)	40	40
Turbidity (FTU)	10	15
Conductivity (as NaCl)	17,500	18,000
Suspended Solids	10	5
pH	7.5	7.43
Acidity: Total	-	-
Free	-	-
Alkalinity: (Total) P($CaCO_3$)	0	0
T(")	93	91
Hardness: Total($CaCO_3$)	3,300	3,200
Calcium($CaCO_3$)	600	590
Halogens: Chlorine	-	-
Chloride	10,000	10,000
Fluoride	-	-
Sulfate	1,500	1,500
Phosphates (Ortho)	0.70	0.68
Nitrate, N	0.24	0.26
Heavy Metals: Iron	0.28	0.32
Chromate	-	-
Oxygen (Dissolved)	-	-
Sulfite	1	1
COD	-	-

---

*All units mg/l unless otherwise specified.

TABLE 31. In-Plant Water Streams at Plant 141

Parameter*	Well Intake Water	Sump to Ponds	Evaporation Pond
Flow	Unable to measure	-	-
Temperature (°C)	19	24.6	17.5
Color (Apparent-APHA)	100	0	35
Turbidity (FTU)	35	10	10
Conductivity (as NaCl)	410	360	790
Suspended Solids	40	4700	0
pH	7.0	8.5	7.7
Acidity: Total	0	0	0
Free	0	0	0
Alkalinity (Total) P	0	0	0
T	475	120	105
Hardness: Total	410	250	500
Calcium	275	112	400
Halogens: Chlorine	0	0	0
Chloride	18.5	20	22.5
Fluoride	0.35	0.6	0.77
Sulfate	78	340	680
Phosphates (Total)	1.6	0.64	0.12
Nitrogen (Total)	0.03	0.18	0
Heavy Metals: Iron	18	9	4
Chromate	0	0.16	0.03
Oxygen (Dissolved)	5.3	5.5	7.9
COD	25	575	70

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*All units mg/l unless otherwise specified.

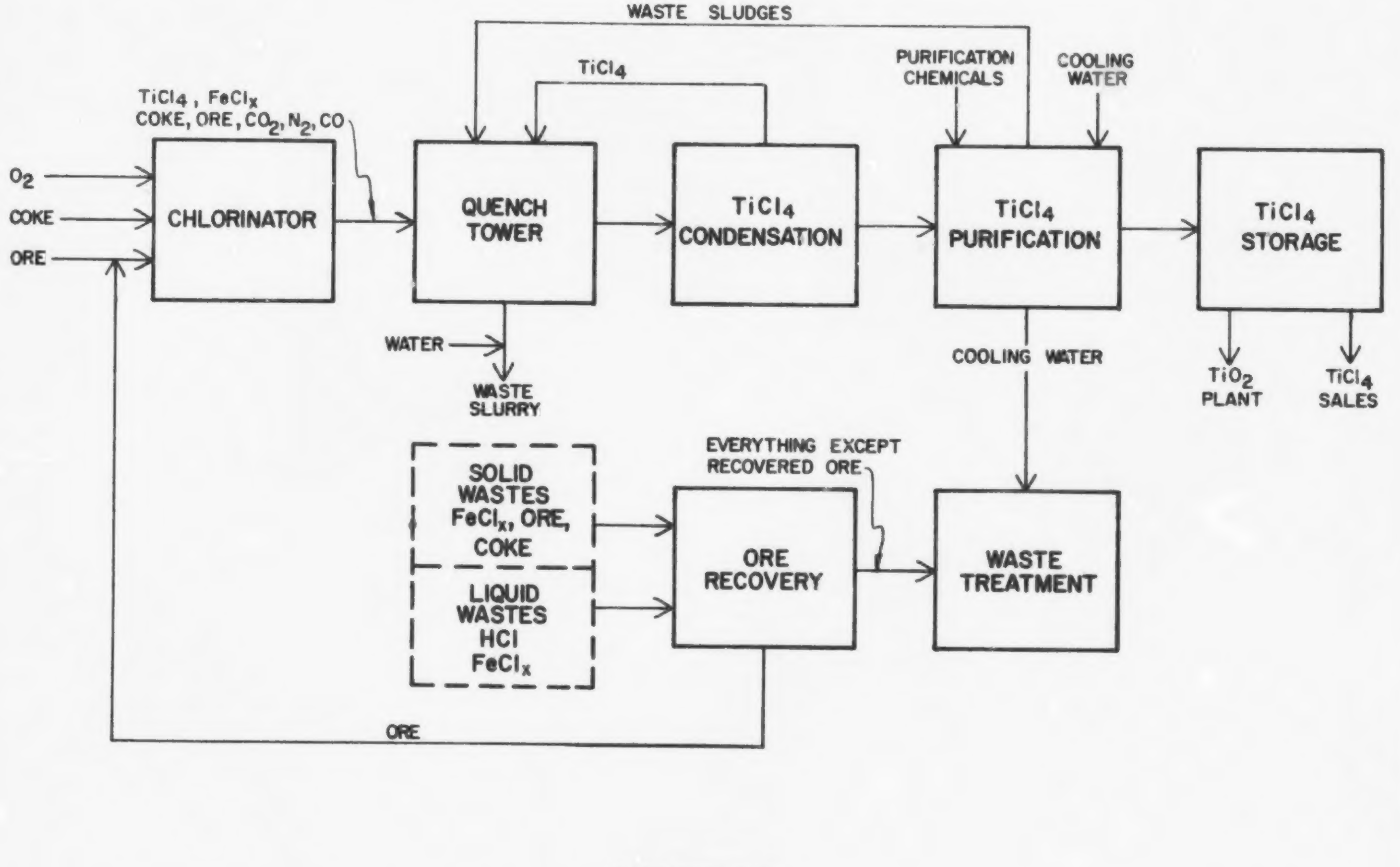
WASTE SLUDGES
$TiCl_4$
PURIFICATION CHEMICALS
COOLING WATER
$TiCl_4$, $FeCl_x$ COKE, ORE, CO_2, N_2, CO
O_2
COKE
ORE
CHLORINATOR
QUENCH TOWER
$TiCl_4$ CONDENSATION
$TiCl_4$ PURIFICATION
$TiCl_4$ STORAGE
WATER
WASTE SLURRY
COOLING WATER
TiO_2 PLANT
$TiCl_4$ SALES
EVERYTHING EXCEPT RECOVERED ORE
SOLID WASTES $FeCl_x$, ORE, COKE
LIQUID WASTES HCl $FeCl_x$
ORE RECOVERY
WASTE TREATMENT
ORE

FIGURE 57
TITANIUM TETRACHLORIDE PORTION OF TITANIUM DIOXIDE PLANT

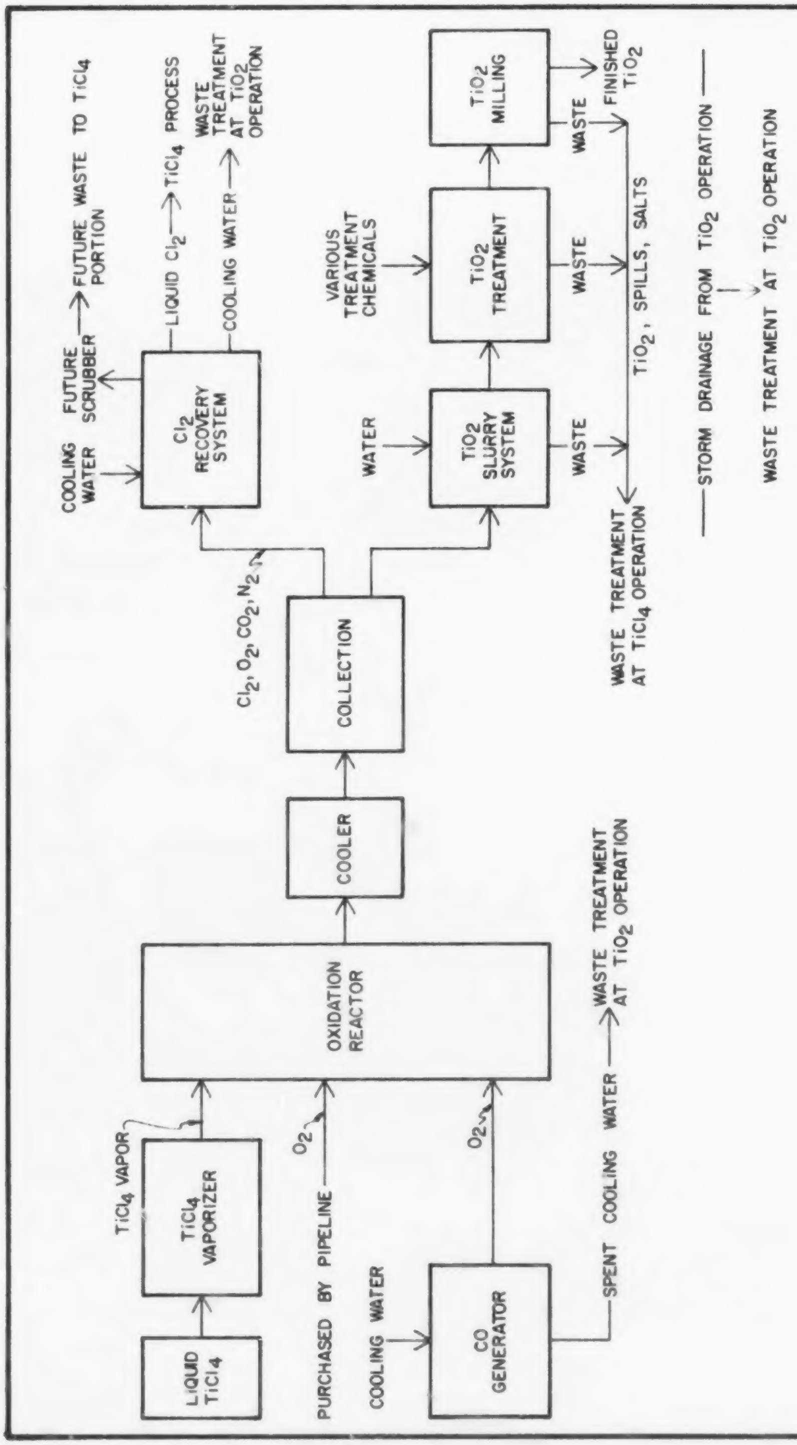
LIQUID TiCl4
TiCl4 VAPORIZER
TiCl4 VAPOR
PURCHASED BY PIPELINE
O2
COOLING WATER
CO GENERATOR
O2
SPENT COOLING WATER
WASTE TREATMENT AT TiO2 OPERATION
OXIDATION REACTOR
COOLER
COLLECTION
Cl2, O2, CO2, N2
COOLING WATER
Cl2 RECOVERY SYSTEM
FUTURE SCRUBBER
FUTURE WASTE TO TiCl4 PORTION
LIQUID Cl2
TiCl4 PROCESS
COOLING WATER
WASTE TREATMENT AT TiO2 OPERATION
WATER
TiO2 SLURRY SYSTEM
VARIOUS TREATMENT CHEMICALS
TiO2 TREATMENT
TiO2 MILLING
FINISHED TiO2
WASTE
WASTE
WASTE
TiO2, SPILLS, SALTS
WASTE TREATMENT AT TiCl4 OPERATION
STORM DRAINAGE FROM TiO2 OPERATION
WASTE TREATMENT AT TiO2 OPERATION

FIGURE 58
TITANIUM DIOXIDE PORTION OF PLANT (CHLORIDE PROCESS)

The raw wastes from plant 009 consist of heavy metal salts, waste coke and hydrochloric acid. In the raw waste stream, these are actually metal chlorides before waste treatment. In detail, the raw wastes are:

Constituents	Ave. kg/kkg (lb/ton) of product
Iron salts (equiv. Fe_2O_3)	58 (116)
Other metal salts (equiv. metal oxides)	58 (116)
Ore	138 (276)
Coke	23 (46)
Titanium hydroxide	29 (58)
TiO_2	40.5 (81)
HCl	227 (454)

Input:

	cu m/day (mgd)	l/kkg (gal/ton)
Lake	11,500 (0.304)	17,100 (4,100)
Municipal	76 (0.020)	1,130 (270)

Use:

			Percent Recycled
Cooling	58,700 (15.5)	876,000 (210,000)	93
Process	6,060 (1.6)	90,500 (21,700)	0
Cleanup	284 (0.075)	4,220 (1,010)	0
Sanitary	38 (0.01)	560 (140)	0
Boiler feed	834 (0.22)	12,500 (3,000)	0

Most of the cooling water is recycled. The waste treatment methods used on the effluent stream, which consist of neutralization, precipitation and settling of heavy metal salts prior to discharge, are shown below. Figures 59 and 60 show the treatment processing at plant 009.

Stream No.	Source	Treatment Methods	Disposal
1	$TiCl_4$ precipitation	Neutralization, settling	Lake
2	Cooling	Neutralization, settling	Lake

Table 32 shows the plant 009 effluents after neutralization and settling treatment. The effluent consists of a neutral pH stream containing dissolved salts (mostly sodium chloride) and low heavy metals concentrations. Table 33 shows verification measurements at this facility.

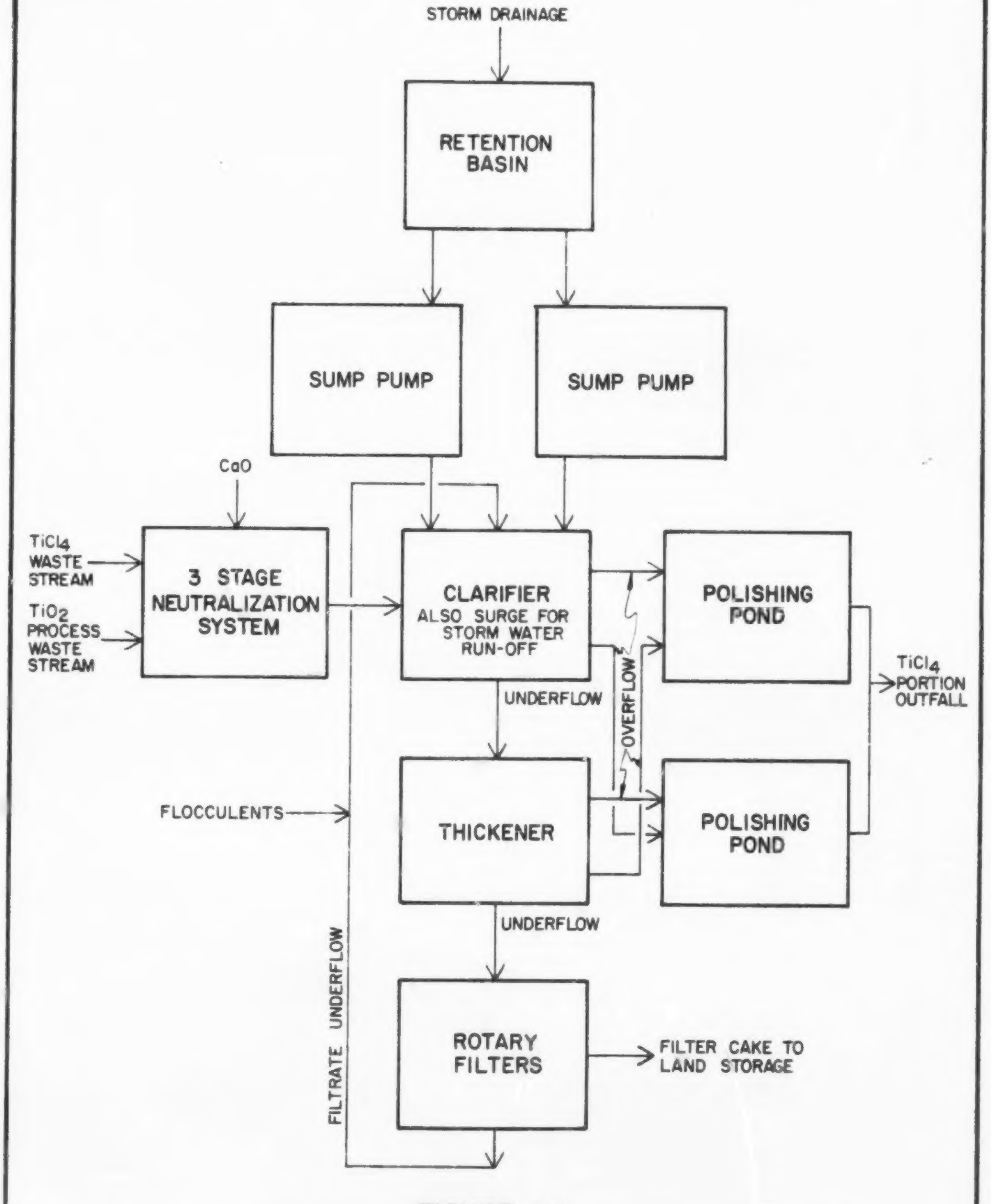
STORM DRAINAGE
RETENTION BASIN
SUMP PUMP
SUMP PUMP
CaO
TiCl4 WASTE STREAM
TiO2 PROCESS WASTE STREAM
3 STAGE NEUTRALIZATION SYSTEM
CLARIFIER ALSO SURGE FOR STORM WATER RUN-OFF
POLISHING POND
TiCl4 PORTION OUTFALL
UNDERFLOW
OVERFLOW
FLOCCULENTS
THICKENER
POLISHING POND
UNDERFLOW
ROTARY FILTERS
FILTER CAKE TO LAND STORAGE
FILTRATE UNDERFLOW

FIGURE 59
TREATMENT, TITANIUM TETRACHLORIDE OF PLANT 009

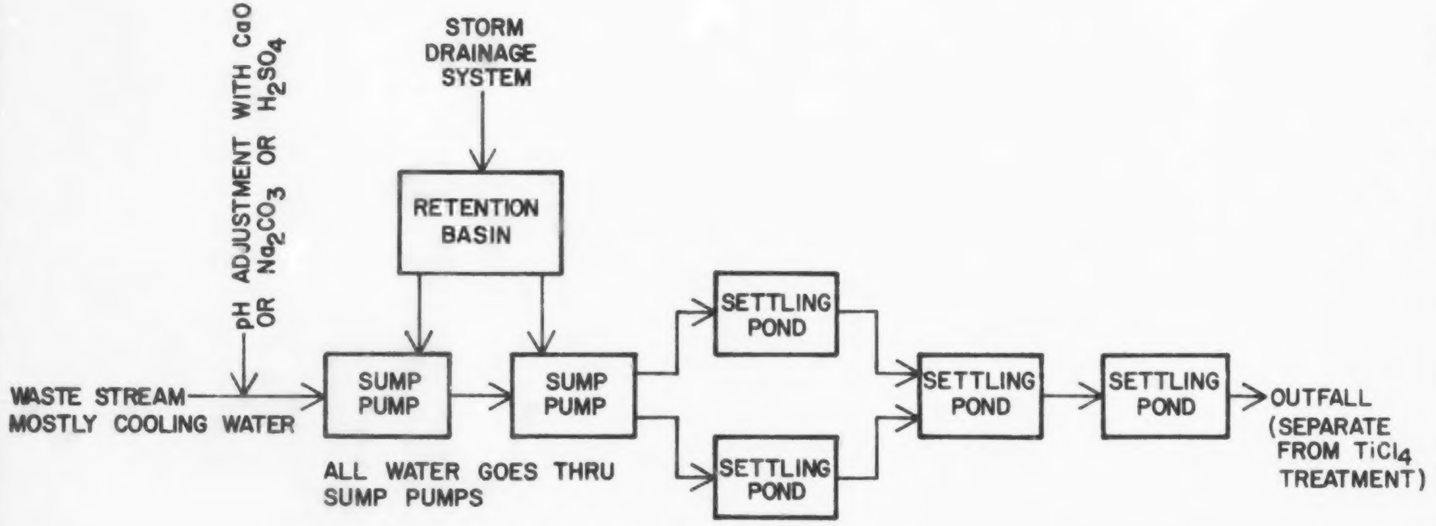
STORM DRAINAGE SYSTEM
RETENTION BASIN
pH ADJUSTMENT WITH CaO OR Na_2CO_3 OR H_2SO_4
WASTE STREAM MOSTLY COOLING WATER
SUMP PUMP
SUMP PUMP
ALL WATER GOES THRU SUMP PUMPS
SETTLING POND
SETTLING POND
SETTLING POND
SETTLING POND
OUTFALL (SEPARATE FROM $TiCl_4$ TREATMENT)

FIGURE 60
TREATMENT, TITANIUM DIOXIDE PORTION OF PLANT 009

TABLE 32. Composition of Plant 009 Effluent Streams After Treatment

Parameter*	Stream No. 1		Stream No. 2	
	Average	Range	Average	Range
Suspended Solids	18	1-50	15	0-40
Total Dissolved Solids	3300	1500-4500	300	180-900
COD	50	40-90	20	5-45
pH	7.8	6.0-9.0	6.8	6.0-9.0
Temperature, °C	16	7-27	16	2-32 (Ambient Temp.)
Organics		None were found		
Turbidity (Jackson Units)	20	10-80	20	10-50
Color (APHA Units)	10	10-20	10	10-20
Chloride	1650	750-2050	50	70-100
Sulfate	--	1-2.5	--	1-2.5
Sulfate	--	--	150	90-450
Iron	0.2	0-3.0	0.2	0.1-1.0
Copper	0.015	0.01-0.03	0.015	0.01-0.03
Chromate	0.01		0.01	
Total Chromium	0.05	0.01-0.15	0.05	0.01-0.15
Arsenic	0.02		0.02	
Mercury	0.001		0.001	
Lead	0.14	0.1-0.19	0.02	0.02

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*mg/l unless otherwise specified

TABLE 33. Verification Data of Plant 009

Parameter*	Lake Intake Water	Effluent Stream #1	Effluent Stream #2
Flow, cu m/day (MGD)	3650 (0.964)	6060 (1.60)	2240 (0.590)
Temperature, °C	9	16	26.5
Color (APHA Units)	100	140	90
Turbidity (FTU)	35	35	30
Conductivity	100 (NaCl)	2100 (NaCl)	170 (NaCl)
Suspended Solids	25.0	10	30
pH	7.9	7.6	6.85
Acidity: Total	N/A	N/A	0 ($CaCO_3$)
Free	N/A	N/A	0 ($CaCO_3$)
Alkalinity (Total) P	0 ($CaCO_3$)	0 ($CaCO_3$)	0 ($CaCO_3$)
T	93 ($CaCO_3$)	22 ($CaCO_3$)	28 ($CaCO_3$)
Hardness: Total	129 ($CaCO_3$)	2600 ($CaCO_3$)	185 ($CaCO_3$)
Calcium	97 ($CaCO_3$)	1920 ($CaCO_3$)	139 ($CaCO_3$)
Halogens: Chlorine	0	0	0
Chloride	36.5	2250	49.5
Fluoride	0	0.3	0.25
Sulfate	32.0	240	175
Phosphates (Total)	1.4	0.025	0.225
Nitrogen (Total)	0.24	0.14	1.3
Heavy Metals:			
Iron	0.225	1.6	0.4
Chromate	0 (Cr+6)	0 (Cr+6)	0 (Cr+6)
Oxygen (Dissolved)	10.8	9.0	6.2

---

*mg/l unless otherwise specified

b) Sulfate process

For the sulfate process, we have examined information on all the existing facilities in the United States. The following description lists the raw wastes and waste segregation practices normally used by the industry and describes planned improved treatments.

In the sulfate process, ground ilmenite ore is digested with concentrated sulfuric acid at relatively high temperature. The acid used is normally about 150 percent of the weight of the ore. In some cases, small amounts of antimony trioxide are also added. The resulting sulfates of titanium and iron are then leached from the reaction mass with water, and any ferric salts present are then reduced to ferrous by treatment with iron scrap to prevent coloration of the final titanium dioxide product.

After these operations, the resulting solutions are clarified, cooled and sent to a vacuum crystallizer. There, ferrous sulfate crystallizes out and is then separated from the mother liquor by centrifugation. This material is either sold or disposed of as a solid waste.

The mother liquor is then clarified by filtration after addition of filter aid and is further concentrated by vacuum evaporation. Seed crystals or other nucleating agents are added, and the concentrated liquor is then treated with steam to hydrolyze the titanyl sufate present. The resulting precipitate is collected by filtration, washed several times and then calcined to yield titanium dioxide. The calcined product is ground, quenched and dispersed in water. The coarse products are separated in a thickener to which caustic soda is added to maintain a constant pH. These coarse particles are reground and further processed to yield a purer product.

Table 34 gives a generalized listing of the raw wastes from titanium dioxide manufacture by the sulfate process. Data in this table are in a form applicable to the effluent from any of the five existing sulfate process plants. Each of these five facilities have slightly different raw wastes due to differences in compositions of the raw ores. Table 35 lists typical ores used in U.S. manufacture of titania, with the Adirondack and Austrailian Ilmenites being typical of ores used with the sulfate process.

Discussion of water use and treatment will be based on one facility, chosen from the five plants. The specific facility used for this modeling discussion is plant 122. A general waste treatment flow chart for this facility is presented in Figure 61 and generalized water usage is:

TABLE 34. Sulfate Process Waste Streams -- Titanium Dioxide Manufacture

1. Dissolving and Filtration	Ore and scrap iron plus flocculants	0.07 x total ore and scrap iron discharged
	H_2SO_4	0.0016 x ore
	Organic Carbon	0.0004 x ore plus 0.1 x C in ore
2. Copperas (if produced)	$FeSO_4.7H_2O$ (as Fe)	(Fe^{+2} + 1.50 Fe^{+3}) in ore minus 0.33 x TiO_2 in ore
	Total Sulfate	1.76 x iron in copperas
3. Strong Acid	$FeSO_4$ (as Fe)	0.67 x (iron in ore minus iron in copperas)
	H_2SO_4	1.07 x ore
	Other ore impurities	0.67 x impurities in ore
	TiO_2	0.03 x TiO_2 in ore
	Organic Carbon	0.0022 x ore plus 0.81 x C in ore
4. Weak Acid	$FeSO_4$ (as Fe)	0.33 x (iron in ore minus iron in copperas)
	H_2SO_4 (Total)	0.53 x ore plus 0.25 x TiO_2 in ore
	Other ore impurities	0.33 x impurities in ore
	TiO_2	0.02 x TiO_2 in ore
	Organic Carbon	0.00025 x ore plus 0.09 x C in ore
5. Vent and Kiln Scrubbing	H_2SO_4	0.01 in ore
6. TiO_2 Losses	TiO_2	0.016 x TiO_2 in ore
	Na_2SO_4	0.03 x TiO_2 in ore

Note: Effluents also contain traces of Pb and Cu from process equipment. Silica and zircon do not react and are discharged with the sludge.

TABLE 35. Typical Ore Analyses* - Titanium Dioxide Manufacture

Constituent (Wt. %)	Adirondack	Australian Ilmenite	Florida Ilmenite	Australian Rutile	Slag
TiO_2	44.5	55.4	64.0	96.3	71.0
FeO	38.0	23.8	3.2		10.9
Fe_2O_3	5.8	16.9	26.9	0.28	
P_2O_5	0.04	0.08	0.21	0.03	0.01
V_2O_5	0.14	0.17	0.13	0.56	0.5
Al_2O_3	1.79	0.94	1.5	0.39	5.7
CaO	0.58	0.02	0.13	0.01	1.0
MgO	2.14	0.27	0.35	0.05	5.0
SiO_2	2.48	0.15	0.3	0.28	5.0
MnO	0.50	0.72	1.35	0.01	0.3
S	0.17	0.01	0.09		0.09
Co	0.02	0.11			
Cr_2O_3	0.01	0.14	0.10	0.20	0.2
ZrO_2			0.07	0.6	
Fe					0.5
C			0.27		
NbO_2			0.11	0.30	
H			0.27	0.02	

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*Blank spaces indicate low impurity level or absence of reliable analytical data. Data from reference 14.

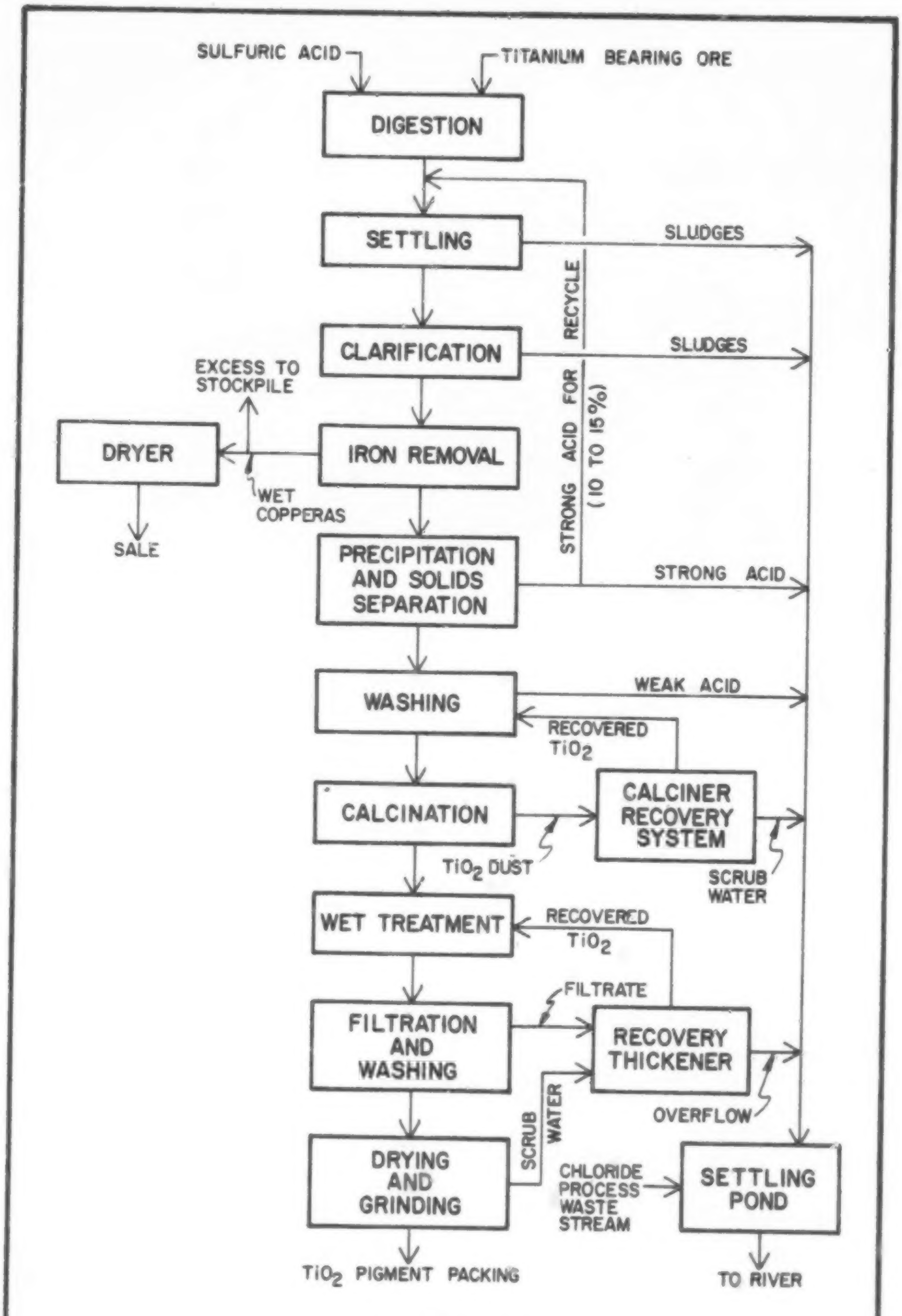
SULFURIC ACID
TITANIUM BEARING ORE
DIGESTION
SETTLING
SLUDGES
RECYCLE
CLARIFICATION
SLUDGES
EXCESS TO STOCKPILE
DRYER
IRON REMOVAL
WET COPPERAS
SALE
STRONG ACID FOR (10 TO 15%)
PRECIPITATION AND SOLIDS SEPARATION
STRONG ACID
WASHING
WEAK ACID
RECOVERED TiO2
CALCINATION
CALCINER RECOVERY SYSTEM
TiO2 DUST
SCRUB WATER
WET TREATMENT
RECOVERED TiO2
FILTRATE
FILTRATION AND WASHING
RECOVERY THICKENER
OVERFLOW
SCRUB WATER
DRYING AND GRINDING
CHLORIDE PROCESS WASTE STREAM
SETTLING POND
TiO2 PIGMENT PACKING
TO RIVER

FIGURE 61
SULFATE PROCESS FLOW DIAGRAM
AT PLANT 122

Type	cu m/kkg of Product (gal/ton)		Recycle
Cooling	284 (68,000)	brackish	0 percent
Cooling	83.6 (20,000)	fresh	90 percent
Process	100 (24,000)		2 percent
Boiler feed	16.7 (4,000)		30 percent

Currently, all of the process water used is fed to a settling pond to remove suspended materials and is then discharged. The process water discharged is from two streams, one from a solids separation part of the process which contains strong (18-22 percent) acid and a second weak acid stream coming from other parts of the process. Both streams are currently mixed before treatment.

In the treatment of wastes, the best approach would be to segregate these two streams and attempt to recover acid values and/or ferrous sulfate from the more acidic stream, while applying neutralization procedures to the other. Considering the strong acid stream first, a possible recovery treatment is first to partially evaporate the waste to effect further precipitation of ferrous sulfate and other metal salts which could be recovered by filtration after cooling. The remaining solution could be further concentrated for other use or recycled to the process.

The weak acid stream, which does not contain sufficient metal or acid values to justify recovery, would be oxidized to convert ferrous salts to the ferric state and then treated with lime to precipitate heavy metals and adjust for pH to contain about 2000 mg/l dissolved $CaCO_3$.

One advantage to this scheme is the possibility of further processing the heavy metal salts recovered by acid concentration. These could possibly be further processed to recover vanadium values, among others. It may be noted that the above-mentioned scheme is a combination of two treatment approaches. The method involving total neutralization and settling is currently being installed at the plant 122 to treat all of the waste streams. Table 36 lists some information on this treatment process.

Effluents from four titanium dioxide sulfate process facilities are listed in Table 37. None of these have discharge pH's in the 6.0-9.0 range for all streams, and all contain 3000 mg/l dissolved solids. In some cases, strong acid streams are currently segregated and this material, in one case, is disposed of by ocean dumping. The neutralization procedure, along with a possible scheme for some acid recovery was discussed earlier in this section.

For the sulfate process, an alternate treatment may consist of raw ore enrichment to remove much of the iron present before the raw material is used in the process. One such potential process

TABLE 36. Future Treatment at Plant 122

Methods	Estimated Installation Time	Estimated Performance
Neutralization of acid to $CaSO_4$ and oxidation of iron, and remove for sale or stockpile (as ferrous sulfate) of process wastes and cooling water	22 mos	Reduce C.O.D to Nil Reduce acidity to Nil Reduce Fe, Mn, V, and Cr to Nil TDS 50 mg/l
Additional settling ponds for cooling waters	22 mos	Reduction of suspended solids formed due to neutralization by 95%

TABLE 37. Partial Discharge Data from TiO_2 Sulfate Plants(1)

	Plant 142 Streams (2)		Plant 046 Streams (3)			Plant 122 Streams			Plant 008
Paramater*	No.1	No.2	No. 1	No. 2	No. 3	No. 1	No. 2	No. 3	No. 1
BOD_5	10	3	6	3	--	--	0.3	0.5	--
COD	71	145	--	--	--	287	42	27	--
pH	8.0	1.2	6.5	5.6	--	1.0	2.6	5.0	5 min
Alkalinity	220	--	--	--	--	--	--	--	--
Total Dissolved Solids	1660	22,371	15,316	21,300	14,000	15,400	3,000	2,700	5,00
Iron	0.02	823	0.5	1.7	31,000	1,000	45	15	100
Sulfate	1,170	12,377	1,617	1,378	131,000	6,800	187	125	--
Chloride	51.5	105	6,394	7,900	--	625	2,480	2,830	--
Acidity	--	11,435	36	--	--	20,000	160	1000	--
Flow, cu m/day	10,200	Combined	20,000	123,400	6,100	20,000	40,900	30,300	
(MGD)	(2.7)	--	(5.5)	(32.6)	(1.6)	(5.5)	(10.8)	(8.0)	

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(1) One plant of one manufacturer is not listed here. Data on titanium dioxid and chromate concentrations were provided.

(2) The corporation owning this facility is currently developing a process for recovery and recycle of the sulfuric acid used. This process is still under testing on the pilot plant scale.

(3) This plant barges its strong acid wastes out to sea for disposal. This method of disposal of highly acid wastes containing large amounts of dissolved heavy metals is not considered satisfactory. Effluent No. 3 is the available data on material dumped at sea.

*mg/l unless otherwise specified

under development at the U.S. Bureau of Mines Reno Research Center involves the smelting of ilmenite ($FeTiO_3$) with coal and sodium borate-titanate slag which contains 40 weight percent titanium dioxide and 0.2 weight percent iron. Over 99 percent of the titanium in the ore is recovered in the slag, while about 90 percent of the iron present is converted to the elemental form. After separation of the iron from the slag, air or oxygen is blown into the molten slag to oxidize the titanium to the tetravalent form which is readily soluble in acid. The molten slag is water quenched and leached in hot water to yield a sodium titanate residue (70 - 90 weight percent TiO_2) in a sodium borate solution. The recovered titanate can then be used in the sulfate process.

Sodium borate in solution is recovered by crystallization and can be recycled to the smelting step. Use of this procedure to provide a sodium titanate feed for the sulfate process eliminates the generation of large amounts of iron sulfate and the inherent problems related to its disposal.

Other methods of ore enrichment under development have been alluded to by the various sulfate process titanium dioxide producers, but details have not been made available.

Substitution of sodium titanate for ilmenite as a sulfate process raw material would lead to a sulfate - bisulfate by-product which could be recovered by crystallization (as is done with ferrous sulfate) for sale. This would eliminate much of the heavy metal salt discharge problems with the sulfate process and also solve the problem of acidic discharges via recovery of a low grade sodium bisulfate by-product for sale or other use.

This approach may prove to be a superior approach to either the neutralization scheme or the acid recovery techniques mentioned earlier. The economics of the above mentioned possible sulfate process modification have not yet been reported. A more detailed evaluation of this possible process must await such an economic presentation.

VERIFICATION SAMPLING AND ANALYTICAL METHODS

Sampling Operations

Two teams of two men each were assigned to the field sampling and measurements operations. Each of the teams was equipped with a station wagon and a 4.7-meter trailer outfitted as a mobile water testing laboratory. The visit of a team to each facility was preceded by a visit to the plant by one of the senior engineers on the project team. During this visit, effluent streams and potential sampling sites were determined and approximate expected stream compositions were established.

The duties of the field team visiting the plant included measurement of flow rate and collection of samples at each designated sampling site. Methods used to determine flow rates varied from stream to stream, but included: (1) Use of existing weirs or installed flow meters; (2) Use of current meter plus dimensional measurements; (3) Direct collection of small outfall streams, with volumetric measurement related to duration of collection; (4) Use of dye tracer to give velocity measurement (plus dimensional measurements).

Since many of the streams of interest could not be approached, the wastes contained therein were sampled after having mixed with one or more other streams.

For most effluent sampling sites, four one-liter samples were taken (one per hour) over a four-hour duration. These samples were then mixed to give a four-liter composite sample. One four-liter grab sample was taken of the water supply to the plant. At the end of the day, a four-liter grab sample was taken at each sampling site (and of the water supply) for backup.

One-half of the four-liter composite sample was used for analyses and tests in the field laboratory. The remaining two liters of composite sample were divided into several samples, some of which were acid-stabilized and transported to an analytical lab for further testing. The sample was split with the plant where it was collected when requested by plant personnel.

The results obtained by the use of the field transportable test methods were, in general, quite reliable. As a routine matter, however, standard test samples were inserted into the analytical program to allow some estimate of the validity of the results reported from the field. The unlabeled standard samples were made up from EPA Reference Samples and presented to the analytical personnel without obvious identification.

The analysis of the samples from various process and discharge streams has been a somewhat complex procedure. This is due, primarily, to the extraordinary variation in flow rates, concentration of solutes and (in particular) the extremely wide range of suspended solids which was encountered.

Pretreatments in the field for the various types of samples were:

(1) Suspended and dissolved solids - none;
(2) Metal ion analysis - addition of 5 ml of concentrated nitric acid per liter of sample;
(3) COD analysis - used immediately in the dichromate reflux apparatus or treated with 1.0 N sulfuric acid;
(4) Nitrogen analysis - used immediately or treated with mercuric chloride for stabilization;

(5) Phosphorus - addition of 40 mg. of mercuric chloride per liter; and
(6) Fluoride - none.

The analytical methods used are those described in EPA's *Methods for Chemical Analysis of Water and Wastes, 1971.*

SECTION VI

SELECTION OF POLLUTANT PARAMETERS

The waste water characterization detailed in the previous Section has been reviewed to determine what waste water constituents are present in significant quantities from the various product subcategories. The criterion used in the selection of pollutant parameters for each subcategory include:

a) Sufficient data is available with regard to the quantities of a pollutant in the raw waste load as well as its treatability by various waste water treatment systems.
b) The pollutant is generally present in the raw waste load in quantities sufficient to cause deletrious effects on the environment.
c) There is demonstrated technology to practicably and economically reduce the concentration of the pollutant.

The following is a discussion of those pollutant parameters which have been selected as the subject of effluent limitations. They have only been selected for those chemical subcategories in which they are generally present in significant quantities.

pH

The term pH is a logarithmic expression of the concentration of hydrogen ions. At a pH of 7, the hydrogen and hydroxyl ion concentrations are essentially equal and the water is neutral. Lower pH values indicate acidity while higher values indicate alkalinity. The relationship between pH and acidity or alkalinity is not necessarily linear or direct.

Waters with a pH below 6.0 are corrosive to water works structures, distribution lines, and household plumbing fixtures and can thus add such constituents to drinking water as iron, copper, zinc, cadmium and lead. The hydrogen ion concentration can affect the "taste" of the water. At a low pH water tastes "sour". The bactericidal effect of chlorine is weakened as the pH increases, and it is advantageous to keep the pH close to 7. This is very significant for providing safe drinking water.

Extremes of pH or rapid pH changes can exert stress conditions or kill aquatic life outright. Dead fish, associated algal blooms, and foul stenches are aesthetic liabilities of any waterway. Even moderate changes from "acceptable" criteria limits of pH are deleterious to some species. The relative toxicity to aquatic life of many materials is increased by changes in the water pH. Metalocyanide complexes can increase a thousand-fold in toxicity with a drop of 1.5 pH units. The availability of many nutrient substances varies with the alkalinity and acidity. Ammonia is more lethal with a higher pH.

The lacrimal fluid of the human eye has a pH of approximately 7.0 and a deviation of 0.1 pH unit from the norm may result in eye irritation for the swimmer. Appreciable irritation will cause severe pain.

Total Suspended Solids

Suspended solids include both organic and inorganic materials. The inorganic components include sand, silt, and clay. The organic fraction includes such materials as grease, oil, tar, animal and vegetable fats, various fibers, sawdust, hair, and various materials from sewers. These solids may settle out rapidly and bottom deposits are often a mixture of both organic and inorganic solids. They adversely affect fisheries by covering the bottom of the stream or lake with a blanket of material that destroys the fish-food bottom fauna or the spawning ground of fish. Deposits containing organic materials may deplete bottom oxygen supplies and produce hydrogen sulfide, carbon dioxide, methane, and other noxious gases.

In raw water sources for domestic use, state and regional agencies generally specify that suspended solids in streams shall not be present in sufficient concentration to be objectionable or to interfere with normal treatment processes. Suspended solids in water may interfere with many industrial processes, and cause foaming in boilers, or encrustations on equipment exposed to water, especially as the temperature rises. Suspended solids are undesirable in water for textile industries; paper and pulp; beverages; dairy products; laundries; dyeing; photography; cooling systems, and power plants. Suspended particles also serve as a transport mechanism for pesticides and other substances which are readily sorbed into or onto clay particles.

Solids may be suspended in water for a time, and then settle to the bed of the stream or lake. These settleable solids discharged with man's wastes may be inert, slowly biodegradable materials, or rapidly decomposable substances. While in suspension, they increase the turbidity of the water, reduce light penetration and impair the photosynthetic activity of aquatic plants.

Solids in suspension are aesthetically displeasing. When they settle to form sludge deposits on the stream or lake bed, they are often much more damaging to the life in water, and they retain the capacity to displease the senses. Solids, when transformed to sludge deposits, may do a variety of damaging things, including blanketing the stream or lake bed and thereby destroying the living spaces for those benthic organisms that would otherwise occupy the habitat. When of an organic and therefore decomposable nature, solids use a portion or all of the dissolved oxygen available in the area. Organic materials also serve as a seemingly inexhaustible food source for sludgeworms and associated organisms.

Turbidity is principally a measure of the light absorbing properties of suspended solids. It is frequently used as a substitute method of quickly estimating the total suspended solids when the concentration is relatively low.

Cyanide

Cyanides in water derive their toxicity primarily from undissolved hydrogen cyanide (HCN) rather than from the cyanide ion (CN^-). HCN dissociates in water into H^+ and CN^- in a pH-dependent reaction. At a pH of 7 or below, less than 1 percent of the cyanide is present as CN^-; at a pH of 8, 6.7 percent; at a pH of 9, 42 percent; and at a pH of 10, 87 percent of the cyanide is dissociated. The toxicity of cyanides is also increased by increases in temperature and reductions in oxygen tensions. A temperature rise of 10°C produced a two- to three-fold increase in the rate of the lethal action of cyanide.

Cyanide has been shown to be poisonous to humans, and amounts over 18 mg/l can have adverse effects. A single dose of 6 mg/l, about 50-60 mg, is reported to be fatal.

Trout and other aquatic organisms are extremely sensitive to cyanide. Amounts as small as 0.1 mg/l can kill them. Certain metals, such as nickel, may complex with cyanide to reduce lethality especially at higher pH values, but zinc and cadmium cyanide complexes are exceedingly toxic.

When fish are poisoned by cyanide, the gills become considerably brighter in color than those of normal fish, owing to the inhibition by cyanide of the oxidase responsible for oxygen transfer from the blood to the tissues.

Chromium

Chromium, in its various valence states, is hazardous to man. It can produce lung tumors when inhaled and induces skin sensitizations. Large doses of chromates have corrosive effects on the intestinal tract and can cause inflammation of the kidneys. Levels of chromate ions that have no effect on man appear to be so low as to prohibit determination to date.

The toxicity of chromium salts toward aquatic life varies widely with the species, temperature, pH, valence of the chromium, and synergistic or antagonistic effects, especially that of hardness. Fish are relatively tolerant of chromium salts, but fish food organisms and other lower forms of aquatic life are extremely sensitive. Chromium also inhibits the growth of algae.

In some agricultural crops, chromium can cause reduced growth or death of the crop. Adverse effects of low concentrations of chromium on corn, tobacco and sugar beets have been documented.

Chemical Oxygen Demand

Certain waste water components are subject to aerobic biochemical degradation in the receiving stream. The chemical oxygen demand is a gross measurement of organic and inorganic material as well as other oxygen-demanding material which could be detrimental to the oxygen content of the receiving water.

Iron

The presence of iron in water causes taste and turbidity problems. It has been shown to be harmful to fish and plants in varying concentrations. Ferric hydroxide has been known to cause detrimental effects to plankton.

Lead

The presence of lead may be a problem in receiving waters. Various oysters and lobsters are known to be adversely effected when exposed to lead in concentrations less than 0.5 mg/l. Lead poisoning in humans has been reported to have been caused by drinking water containing less than 0.1 mg/l lead.

Mercury

Mercury has been shown to be deletrious to the environment in low concentrations. Many aquatic organisms are adversely affected by mercury concentrations of less than 0.01 mg/l.

Total Organic Carbon

Soluble organics may cause utilization or depletion of dissolved oxygen by the activity of aerobic bacteria. They may also impart undesirable tastes and odors to a water supply. For example, phenolics are a special nuisance in drinking water supply, particularly after chlorination, because of the very low concentrations (less than 0.002 mg/l) which result in taste and odor detection.

The quantity of soluble organics can be measured as BOD, COD or TOC (Total Organic Carbon). However, each of these parameters will measure differing amounts of soluble organics. For example, many organic compounds which are dichromate oxidizable (COD) are not biochemically oxidizable (BOD). Also, many inorganic substances such as sulfides, nitrites, etc., are oxidized by dichromate (COD) which may be misleading when estimating the organic content of the waste water. The total organic carbon determination oxidizes the carbon atoms of organic molecules to carbon dioxide, and measures the amount of carbon dioxide quantitatively. It lacks the many variables present in the COD and BOD analyses, resulting in more reliable and reproducible results for organic determinations.

In general, other pollutant parameters have not been selected because they are present in relatively small quantities. There are a few notable exceptions, however. Dissolved salts, such as chlorides and sulfates, are often present in large quantities. Treatment technologies to reduce or remove these constituents may be expensive and in many cases the costs are prohibitive at this time.

Titanium dioxide manufacture generates a waste stream containing many types of metal ions. Treatment and removal of iron will coincidently remove other metals to acceptable levels. Therefore, other waste water constituents have not been the subject of effluent guidelines, even though they may be present in large quantities.

SECTION VII

CONTROL AND TREATMENT TECHNOLOGY

Alternative control and treatment technologies for each chemical subcategory are discussed in detail on the following pages.

SPECIFIC CONTROL AND TREATMENT PRACTICES IN THE INDUSTRY

Aluminum Chloride

Direct chlorination of aluminum to produce aluminum chloride is a relatively simple process. Plants are small (9 to 18 metric tons/day). There is no process water involved, nor usually any cooling water. The only source of water wastes is from equipment used to treat air-borne wastes such as aluminum chloride dust around the packing station and aluminum chloride and chlorine from the air-cooled condensers.

In some plants, run on the aluminum-rich side (white or gray aluminum chloride), there is very little chlorine in the discharge from the air-cooled condenser. Also, the gas volume from the condenser is such that only a very small quantity of aluminum chloride is discharged. In such plants there may be no air pollution control provision. One exemplary plant operates in this fashion. In plants operating on the chlorine-rich side (yellow aluminum chloride), water scrubbing of the air condenser discharge gases is needed.

At least three practicable, economically feasible, and low energy air pollution control approaches are available:

(1) No air or gas treatment for gray or white aluminum chloride.
(2) Gas scrubbing and sale of scrubber wastes. This approach is taken by an exemplary plant of this study.
(3) Gas scrubbing followed by chemical treatment to precipitate aluminum hydroxide and convert chlorine to sodium chloride. Technology available from the chlor-alkali and titanium dioxide chloride process may be applied.

Aluminum Sulfate

Current typical treatment involves use of a settling pond to remove muds followed by neutralization of residual sulfuric acid prior to discharge.

Two exemplary plants (049 and 063) have closed loop waste-water systems. Suspended solids are removed in settling vessels and ponds and the clear overflow is returned to the manufacturing process.

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TABLE 38. Summary of BPCTCA and BATEA

Chemical	BPCTCA Guideline	Best Practicable Control Technology Currently Available BPCTCA	BATEA Guideline	Best Available Technology Economically Achievable BATEA
Aluminum Chloride (Anhydrous)	No discharge of pollutants in process waste waters	(1) No water scrubbers for white or grey aluminum chloride production (2) For yellow aluminum chloride production, gas scrubbing and sale of scrubber wastes as aluminum chloride solution; or (3) Gas scrubbing followed by chemical treatment to precipitate aluminum hydroxide and and recycle	Same as BPCTCA	Same as BPCTCA
Aluminum Sulfate	No discharge of pollutants in process waste waters	(1) Settling pond and reuse	Same as BPCTCA	Same as BPCTCA
Calcium Carbide	No discharge of pollutants in process waste waters	(1) Dry dust collection system	Same as BPCTCA	Same as BPCTCA
Hydrochloric Acid Chlorine Burning	No discharge of pollutants in process waste water	(1) Acid containment and isolation with centralized collection of acid wastes; and reuse	Same as BPCTCA	Same as BPCTCA
Hydrofluoric Acid	No discharge of pollutants in process waste waters	(1) Acid containment and isolation; and reuse	Same as BPCTCA	Same as BPCTCA
Sodium Bicarbonate	No discharge of pollutants in process waste water	(1) Evaporation and product recovery; or (2) Recycle to process;	Same as BPCTCA	Same as BPCTCA
Sodium Chloride (Solar Process)	Return of unused salts to the brine source	(1) Good housekeeping to prevent contamination of waste salts	Same as BPCTCA	Same as BPCTCA
Sodium Silicate	TSS 0.005	(1) Storage of wastes in an evaporation pond; or (2) Ponding and clarification	No discharge of pollutants in process waste water	Ponding or clarification and recycle of the treated waste water
Sulfuric Acid (Sulfur Burning Contact Process)	No discharge of pollutants in process waste water	(1) Acid containment and isolation with recycle to process or sale as weak acid;	Same as BPCTCA	Same as BPCTCA

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TABLE 38. Summary of BPCTCA and BATEA (continued)

Chemical	BPCTCA Guideline	Best Practicable Control Technology Currently Available BPCTCA	BATEA Guideline	Best Available Technology Economically Achievable BATEA
Lime	No discharge of pollutants in process waste water	(1) Dry Bag Collection System; or (2) Treatment of scrubber water by ponding and clarification and recycle	Same as BPCTCA	Same as BPCTCA
Nitric Acid	No discharge of pollutants in process waste water	(1) Acid containment and isolation and reuse	Same as BPCTCA	Same as BPCTCA
Potassium (Metal)	No discharge of pollutants in process waste water	(1) No process water used in manufacture	Same as BPCTCA	Same as BPCTCA
Potassium Dichromate	No discharge of pollutants in process waste water	(1) Replacement of barometric condensers with non-contact heat exchangers; recycle of process liquor	Same as BPCTCA	Same as BPCTCA
Potassium Sulfate	No discharge of pollutants in process waste water	(1) Evaporation of brine waters with recovery of magnesium chlorine; or (2) Reuse of brine solution in process in place of process water;	Same as BPCTCA	Same as BPCTCA

Chemical	Flow liters/kkg	Limitation kg/kkg TSS	Limitation kg/kkg Other	Best Practicable Control Technology Currently Available BPCTCA	Flow liters/kkg	Limitation kg/kkg TSS	Best Available Technology Economically Achievable BATEA
Calcium Chloride (Brine Extraction)	330	0.0082	-	(1) Settling pond or clarification	No discharge of pollutants in process waste water		Same as BPCTCA plus (1) Replacement of barometric condensers with noncontact heat exchangers; and additional recycle
Hydrogen Peroxide (Organic)	16,000	0.40	0.22 TOC	(1) Isolation and containment of process wastes; oil separation and clarification	No discharge of pollutants in process waste water		(1) Chemical decomposition for peroxide removal (2) Carbon adsorption for organic removal
Sodium (Metal)	9,000	0.23	-	(1) Settling pond; and (2) Partial recycle of brine waste solution after treatment	No discharge of pollutants in process waste water		100% brine recycle and reuse or sale of spent sulfuric acid
Sodium Chloride (Solution Mining)	6,400	0.15	-	(1) Containment and isolation of spills, packaging wastes, scrubbers, etc; partial recycle to brine cavity	No discharge of pollutants in process waste water		Same as BPCTCA plus (1) Replacement of barometric condensers with noncontact heat exchangers
Sodium Sulfite	630	0.016	1.7** COD (As Cr_2O_7	(1) Air oxidation of sodium sulfite wastes to sodium sulfate -- 94% effective, and final filtration to remove suspended solids	No discharge of pollutants in process waste water		Same as BPCTCA plus recovery of waste sodium sulfate
Soda Ash (Sodium Carbonate) Solvay Process	6,900	0.17	-	(1) Settling ponds	6,900	0.10	(1) Settling ponds and clarification

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TABLE 38. Summary of BPCTCA and BATEA (continued)

Chemical	BPCTCA Guideline			Best Practicable Control Technology Currently Available BPCTCA	BATEA Guideline	Best Available Technology Economically Achievable BATEA
	Flow liters/kkg	Limitation kg/kkg				
		TSS	Other			
Hydrogen Peroxide (Electrolytic)	95	0.0025	0.002 CN^-	(1) Ion exchange to convert sodium ferrocyanide to ammonium ferrocyanide which is then reacted with hypochlorite solution to oxidize it to cyanate solutions; and (2) Settling pond or filtration to remove catalyst and suspended solids	No discharge of pollutants in process waste water	(1) Same as BPCTCA plus segregation of waste water from cooling water and evaporation of the waste stream and recycle of the distillate
Sodium Dichromate and Sodium Sulfate	8,900	0.22	0.0005 Cr^{+6} 0.0044 Cr(total)	(1) Isolation and containment of spills, leaks, and runn off; and (2) Batchwise treatment to reduce hexavalent chromium to trivalent chromium with NaHS, plus precipitation with lime or caustic; and (3) Settling pond with controlled discharge	No discharge of pollutants in process waste water	Same as BPCTCA plus (1) Evaporation of the settling pond effluent with recycle of water and land disposal or recovery of solid waste
Chlor-alkali (Diaphragm Cell)	3,300	0.32	0.0025 Pb	(1) Asbestos and cell rebuild wastes are filtered or settled in ponds then land dumped; and (2) Chlorinated organic wastes are incinerated or land dumped; and (3) Purification muds from brine purification are turned to salt cavity or sent to evaporation pond/settling pond; and (4) Weak Caustic—brine solution from the caustic filters is partially recycled	No discharge of pollutants in process waste waster	Same as BPCTCA plus (1) Reuse or sell waste sulfuric acid (2) Catalytic treatment of the hypochlorite waste and reuse or recovery (3) Recycle of all weak brine solutions (4) Conversion to stable anodes
Chlor-alkali (Mercury Cell)	21,000	0.32	0.00014 Hg	(1) Cell rebuilding wastes are filtered or placed in settling pond, then used for landfill; and (2) Chlorindated organic wastes are incinerated or placed in containers and land dumped; and (3) Purification muds from brine purification are returned to brine cavity or sent to evaporation/settling ponds; and (4) Partial recycle of brine waste streams; and (5) Recovery and reuse of mercury effluent by curbing, insulation and collection of mercury containing streams, then treatment with sodium sulfide	No discharge of pollutants in process waste water	Same as BPCTCA plus (1) Reuse or recovery of waste sulfuric acid (2) Catalytic treatment of the hypochlorite waste and reuse or recovery (3) Recycle of all weak brine solutions

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TABLE 38. Summary of BPCTCA and BATEA (continued)

Chemical	BPCTCA Guideline			Best Practicable Control Technology Currently Available BPCTCA	BATEA Guideline		Best Available Technology Economically Achievable BATEA
	Flow liters/kkg	Limitation kg/kkg TSS	Other				
Titanium Dioxide (Chloride Process)	90,500	2.2	Iron 0.36	(1) Neutralization with lime or caustic; and (2) Removal of suspended solids with settling ponds or clarifier-thickener; and (3) Recovery of by-products .g., V, Al, Si, Cr, Mn, Nb & Zr.	TSS 1.3	Iron 0.18	Same as BPCTCA plus additional clarification and polishing
Titanium Dioxide (Sulfate Process)	210,000	10.5	Iron 0.84	(1) Neutralization with lime or caustic; and (2) Removal of suspended solids with settling ponds or clarifier-thickener; and (3) Recovery of by-products	TSS 5.3	Iron 0.42	Same as BPCTCA plus addition clarification and polishing

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*Monthly average values. To convert from metric units to English units (lbs/ton), multiply the above values by 2.

**COD of 2720 mg of dichromate ion per liter

Calcium Carbide

There is no process water involved in the production of calcium carbide. Ancillary water wastes such as cooling tower blowdowns and ion exchange regenerants are often present. There may also be water-borne wastes from air pollution control equipment.

Water-borne wastes from air-borne waste control equipment may be avoided by use of dry bag collector systems. Unlike aluminum chloride, the air-borne wastes from the calcium carbide process are all dusts -- coke and coal fines, limestone powder and calcium carbide from the packing station. Coke, coal and limestone fines, which constitute a significant fraction of the feed materials, may be profitably returned to the system. One plant uses only dry bag collectors and recycles the collected fines to the furnace.

Dry bag collection of air-borne fines eliminates waterborne wastes and makes it possible to reuse these fines. It also significantly reduces energy requirements by avoiding high energy drying costs needed for recovery of water wastes.

Calcium Chloride

This chemical is obtained both from soda ash wastes and from natural salt deposits. The soda ash produces large amounts of calcium chloride as a by-product. Unreacted sodium chloride and other dissolved solids are present in this waste stream. After calcium chloride is extracted from this waste stream, the remaining calcium chloride, sodium chloride and other dissolved solids may be returned to the waste stream of soda ash manufacture. Extraction of calcium chloride from natural salt deposits is carried out in a major chemical complex and is scheduled within the next six months to be brought to virtually a zero process waste water pollutant discharge. Since both processes are dissimilar, there are no typical practices. The two major producers differ widely in their treatment approach.

From the soda ash process, recovery of calcium chloride is considered as a zero discharge process similar to sodium sulfate from the sodium dichromate process. There are no additional wastes generated as a result of this recovery.

The natural salt process, on the other hand, utilizes the integrated nature of the complex where it is produced to take advantage of every normal waste. Sodium chloride goes to chlor-alkali facilities. Magnesium chloride, which is often difficult to dispose, is isolated and used for other processes. Consequently this process for making calcium chloride also has no effluent in the particular complex where it is made. This is a good example of the previously discussed principle that wastes from a complex should never be greater than the sum of the individual plants and usually will be significantly less.

Calcium Oxide and Calcium Hydroxide

The process for producing calcium oxide involves no water-borne wastes. Waste water treatment is required only when wet scrubbers are used to remove entrained dust from the gaseous effluent.

Practices evidently vary from one plant to another as far as air pollution control practices are concerned. Some plants have no facilities for air-borne wastes, others use water scrubbers or dry bag collectors.

Water-borne wastes from air-borne waste control equipment may be avoided by use of dry bag collector systems. Unlike aluminum chloride, the air-borne wastes from the calcium oxide process are all dusts. This dust may be profitably returned to the system. The exemplary plant of this study uses only dry bag collectors and recycles collected fines.

Dry bag collection of air-borne fines not only eliminates water-borne wastes and makes it possible to reuse these fines, but it also significantly reduces energy requirements by avoiding high energy drying costs needed for recovery of water wastes.

If wet scrubbers are used, the scrubber solution may be discharged to a settling pond or vessel and recycled to the scrubbing system after sedimentation of suspended solids.

Chlorine and Sodium or Potassium Hydroxide

Chlorine is produced by three major processes: mercury cells, diaphragm cells and Downs Cells. The other chemicals produced are sodium (Downs Cell only), sodium hydroxide and potassium hydroxide, variously. There is also quite often a direct burning hydrochloric acid plant in the complex.

The following chlorine discussion includes mercury and diaphragm cell productions. Downs Cell operation will be discussed under sodium, but the chlorine-based wastes are the same as for the mercury and diaphragm cells.

The chlor-alkali industry uses salt (sodium chloride or potassium chloride) as its raw material. Transformations of all sodium and chlorine chemicals can and have been made in chlor-alkali plants. There is a fortunate situation from the standpoint of waste reduction and zero discharge. In contrast, for example, are the soda ash process which produces large quantities of calcium chloride and the potassium dichromate process which produces large quantities of sodium chloride. Currently, there is only a limited use for these waste products. Examples of how waste conversions can be made in the chlor-alkali process are given in the following equations:

(1) $2NaCl \longrightarrow 2Na + Cl_2$
(2) $2Na + 2H_2O \longrightarrow 2NaOH + H_2$
(3) $2NaOH + Cl_2 \longrightarrow NaOCl + NaCl + H_2O$
(4) $2NaOCl + Cat. \longrightarrow 2NaCl + O_2$
(5) $Cl_2 + H_2 \longrightarrow 2HCl$
(6) $HCl + NaOH \longrightarrow NaCl + H_2O$

Equations (1) and (2) show the product formations. Equation (3) represents tail gas scrubbing operations to remove chlorine gas from air effluents from the plants. Equation (4) shows conversion of sodium hypochlorite back to salt raw reactant materials. Equation (5) eliminates waste chlorine gas by direct burning of chlorine to produce hydrochloric acid. Equation (6) uses hydrochloric acid to neutralize waste sodium hydroxide, thereby producing salt for return to the system. Provided the water-borne waste streams are kept isolated from much larger cooling water streams, control and treatment techniques are entirely feasible.

Salt impurities have to be removed by precipitations before the brine solutions can be used in the cells. Treatment with soda ash, sodium hydroxide, and sometimes barium chloride, removes calcium, magnesium and sulfate ions as calcium carbonate, magnesium hydroxides and barium sulfates, respectively. The precipitated muds may be removed in ponds or clarification tanks. The muds may be disposed of by land dumping or fill.

Brine and sulfuric acid wastes may be neutralized with lime or sodium hydroxide, and ponded for reduction of suspended solids.

Water-borne mercury in the mercury cell process may be treated and removed by a variety of processes, usually employing precipitation of mercury sulfides, followed by mercury recovery by roasting or chemical treatment processes. Plants with typical recovery systems reduce mercury in the plant effluent to 0.11 to 0.22 kg/day (0.25-0.50 lb/day).

Total waste reduction depends on in-process control, isolation, treatment and reuse. There is no known problem which has not been solved by at least one plant of this survey.

Mercury cells are inherently "cleaner" processes than the diaphragm cells. Diaphragm cells have asbestos diaphragm deteriorations with suspended asbestos wastes. These have to be filtered out or allowed to settle in ponds. Sodium hydroxide produced in diaphragm cells has sodium chloride and other wastes and has to be purified for many uses.

A sodium sulfate purge, made by back-washing the precipitated salt slurry on the filter during the evaporation concentration of sodium hydroxide, is also needed to ensure satisfactory diaphragm cell operation. This sulfate purge can be handled by removing it from the system and using it elsewhere (as is done by exemplary diaphragm cell plant 057), by returning it for sulfate removal in the brine purification, or by recovery of sodium sulfate for sale.

Another waste from the diaphragm process, but not the mercury cell, is organic waste from the graphite anode. These are currently land disposed by the exemplary diaphragm cell plant, but are allowed to go out in waste streams at others.

Waste sulfuric acid from the chlorine-drying step may be used for neutralizations in other processes, sale, shipment to a regen sulfuric acid plant or concentration.

Collected chlorine gas for abatement of air-borne wastes can be burned to produce hydrochloric acid or converted to sodium chloride as discussed earlier.

Diaphragm cells are prone to develop cracks around their anode protective resin seals and lead salts from the underlying lead mountings can get into the effluents. Metal anodes can eliminate this problem and at a reported significant reduction in required cell electrical energy load.

The mercury cell, although "cleaner" than the diaphragm process, has a major waste problem in the form of mercury in the water-borne wastes. Major expenditures (discussed quantitatively in Section VIII) and in-process modifications have been made to alleviate this problem. Three plants discussed in section V reduce their mercury discharge to 0.00057, 0.000069 and 0.00007 kg/kkg (0.0011, 0.000137, 0.00014 lb/ton). A small, 140 ton/day plant has reportedly reduced its mercury discharge to an average of 0.000143 kg/kkg (0.000286 lb/ton). These low levels are accomplished by isolation of mercury-containing waste streams and chemical treatment of these streams.

Although no specific mention has been made of potassium hydroxide production, the same principles hold except that potassium is substituted for sodium.

By employing extensive treatment, control, recycle, and recovery, the chlor-alkali process may be operated with no discharge of process waste water pollutants to navigable waters.

Hydrochloric Acid

The only process considered in this study is chlorine burning. Only about ten percent of the U.S. production comes from this process. Most hydrochloric acid is produced as a by-product of other processes. The chlorine-burning process is a simple one and capital equipment is relatively inexpensive. The process fits well with chlor-alkali complexes where low-cost or waste chlorine (and possibly hydrogen from mercury cells) is readily available.

There is no water-borne process waste during normal operation. A small amount of chlorine and hydrochloric acid wastes is developed during startup. Neutralization with sodium hydroxide can be followed by forwarding the neutralized stream to other chlor-alkali complex uses such as make-up water for brine solutions used in mercury or diaphragm cells. The size of the waste load, excluding that from the air-borne hydrogen chloride treatment, is small - 0.5 to 1.0 kg/kkg.

Since there are no process wastes, spills, leaks, contributions from air-borne hydrogen chloride waste treatment equipment, and startup and upset wastes are the only concerns. Base treatment and control of these small miscellaneous wastes consists of neutralization with available sodium hydroxide followed by discharge to surface water.

Leaks, spills and startup wastes may be minimized by good housekeeping, operation, equipment maintenance and production planning. These wastes are not at this time directly related to a unit of production and may need to be limited on a case by case basis. To reduce water-borne wastes, containment and isolation techniques are required. Dikes, dip pans and other devices are used to control leaks and spills. Centralized collection and neutralization with sodium hydroxide can be followed by forwarding the neutralized stream to other chlor-alkali complex uses such as make-up water for brine solutions used in mercury or diaphragm cells. The size of the waste load, excluding that from the air-borne hydrogen chloride treatment, is small - 0.5 to one kg/kkg.

Hydrofluoric Acid

Hydrofluoric acid sells for approximately $550/kkg. Therefore, the incentive for containment and recovery of leaks, spills and other product losses is understandably greater than for the other mineral acids. By the nature of the process, large quantities of cooling water are required. This is in the non-contact category, however, such that water-borne process waste loads are small.

Neutralization of sulfuric and hydrofluoric acid wastes with lime, followed by removal of precipitated calcium sulfate and calcium fluoride in settling ponds, reduces fluorides to 18 mg/l and calcium sulfate to approximately 2000 mg/l in treated water streams.

Segregation of the leaks, spills and sulfuric acid-containing wastes from the cooling water reduces the quantity of water which has to be treated. Also by in-process changes, such as using stoichiometric quantities of sulfuric acid in the process reactor, the sulfuric acid may be eliminated from the process waste water stream.

Lime treatment of the isolated wastes and settling pond removal of the precipitate reduces the fluoride content of this small stream to approximately 10 mg/l. This procedure gives waste with less than 0.5 kg total dissolved solids kkg (1 lb/ton) of hydrofluoric acid. This treatment makes closed cycle operation possible.

There are no air pollution problems for this process, but massive calcium sulfate solid wastes (3400-4250 kg/kkg (6800-8500 lb/ton) of hydrofluoric acid) from the process reactor give both land disposal and rainwater runoff problems. Storage piles of this calcium sulfate should be located and contained so that materials such as calcium sulfate and residual lime or sulfuric acid are not conveyed by rainwater runoff to surface or underground fresh water streams.

Hydrogen Peroxide

a) Organic process

The organic process effluent generally contains waste hydrogen peroxide plus organic solvent used in the process. The nature of this solvent is considered a trade secret.

The hydrogen peroxide waste may be decomposed with scrap iron. The organic solvent may be removed by skimming the insoluble layer off the top of the water stream. The effluent may then be passed into a settling pond for removal of suspended solids or organic solvent interaction with suspended solids from other processes. Additional isolation, containment and treatment of wastes with scrap iron for peroxides and skimming separation for organics further reduces the waste loads.

Organics may be removed from this waste water stream by biological digestion or carbon adsorption treatment.

b) Electrolytic process

The electrolytic process for making hydrogen peroxide is represented by a single U.S. plant (100). Its effluent has practically the same composition as the incoming water, because the relatively very small amount of process water discharged is combined with the very large cooling water stream. Present levels were accomplished by in-process controls. The total water flow into the plant is about 41,600 cu m/day or 3,470,00 l/kkg

(11,000,000 gal/day or 11,000,000 gal/ton). 75.7 cu m/day or 6300 l/kkg (20,000 gal/day or 1830 gal/ton) is treated by ion exchange and used for boiler feed and process water. Discharges of this waste include 3.8 cu m/day or 316 l/kkg (1000 gal/day or 92 gal/ton) of ion exchange blowdown, 26.5 cu m/day or 2200 l/kkg (7000 gal/day or 640 gal/ton) of boiler blowdown and 1.1 cu m/day or 95 l/kkg (290 gal/day or 27.6 gal/ton) of process water effluent. This latter stream may be eliminated by simple procedures such as total evaporation which is economically feasible because of the small quantity.

Nitric Acid

There are generally no water-borne process wastes. There are usually no water-borne wastes from air pollution abatement practices. Cooling water requirements are high. Minor water-borne wastes are due to leaks, spills and washdowns and ancillary systems such as cooling towers.

Provisions may be made for handling and neutralizing spills and leaks. Neutralization can be done with limestone, oyster or clam shells, lime or sodium hydroxide. Collected leaks, spills and washdowns may be returned to the process.

Diking of tanks, pump areas, loading and washing areas may be combined with isolation and reuse of leaks, spills and washdowns. Diking of large tanks should be sufficient for complete containment. Emergency ponds should be provided for major upsets. Limestone or seashell pond linings and ground coverings may be used for neutralizations.

Potassium Metal

There are no water-borne wastes from this process.

Potassium Chromates

Potassium dichromate is made from the reaction of sodium dichromate with potassium chloride. There is none of the massive ore waste present as in the sodium dichromate process. The only water-borne wastes from the major U.S. production facility emanate from contamination of once-through cooling water used in the barometric condensers. These are scheduled for replacement in 1974 by heat exchangers using non-contact cooling water. This will result in no discharge of waterborne wastes.

Potassium Sulfate

The exemplary plant for production of potassium sulfate is plant 118. It is a closed cycle plant where water recovery is accomplished by distillation of 1,500 cu m/day (400 gpd).

Sodium Bicarbonate

Typical treatment practices involve the settling of suspended solids in ponds before discharging the effluent to surface waters.

The untreated effluent from this process is essentially sodium carbonate in solution. In a complex, use for this solution may be made, probably at lower cost than for recovery. Present waterborne wastes are a relatively low 6.5 kg/kkg (13 lb/ton) of product.

By keeping the waste stream small and the solids level high, evaporative techniques are feasible without undue expense. The evaporation process yields demineralized water for boilers, plus recovered product worth $36/kkg ($32/ton). An alternative approach would involve total recycle.

Sodium Carbonate

The Solvay Process for making sodium carbonate (soda ash) is an old one dating back to the late 1800's. The Solvay plants are also old, the last U.S. plant being built in the 1930's.

The Solvay Process discharges more poundage of waste into surface water (solid basis) than any other chemical of this study (sodium chloride producers deep-well or store most of their effluent). The only redeeming feature is the relatively low toxicity of the waste.

Present treatment of water-borne wastes consists of removing most of the suspended calcium carbonate and other solids in unlined settling ponds followed by discharge to surface water. Adjustment for pH may or may not be done prior to this discharge.

The water-borne wastes from the Solvay Process are suspended and dissolved solids. The suspended solids are removed effectively by settling ponds and polish filtering can be done, if necessary, to reduce total suspended solids levels to 25 mg/l.

Dissolved solids are generally present in high concentrations. There are many treatment technologies available which can be used to eliminate the dissolved solids from the water effluent. However, most of them are not economically practical for the Solvay Process. Also, the geographical location of the plant has a major bearing on the treatment and disposal feasibility and costs.

A new plant of the Solvay Process is very unlikely to be considered. If a new Solvay Process plant were to be built, the process itself would likely be revised. Process modifications now in the laboratory or pilot plant stages would have to be investigated and developed for commercial feasibility. The major area of revision would be in the recovery of ammonia from ammonium chloride. Use and recovery of magnesium hydroxide or decomposition of ammonium chloride to ammonia and chlorine are two such modifications that have been proposed. Recovery and reuse of the excess sodium chloride in the waste effluent could be accomplished by evaporation and crystallization techniques similar to those for the salt industry.

Sodium Chloride

Waste disposal is usually accomplished by pumping the brine wastes back into the well or mine when sodium chloride is made by the brine extraction process. In the solar evaporation process, brine wastes are normally returned to the source of the salt solution. Storage and recovery of magnesium and potassium salts is technically feasible, but appears uneconomical in most instances.

Sodium Dichromate and Sodium Sulfate

Typical treatment is to reduce the hexavalent chromium ion in the waste to trivalent chromium, remove the suspended solids in a settling pond, and discharge the clear solution to surface water. Ferrous chloride is often used as a reducing agent.

An exemplary chromium treatment and control plant (184) includes isolation of all chromium-containing, water-borne wastes from cooling water, collection of these wastes in tanks, batchwise treatment for hexavalent chromium reduction, and pond settling of suspended solids. The hexavalent chromium content remaining after treatment is very low. Provisions are made in this plant for collection and treatment of rainwater.

Although the treatment and control technologies described above are excellent for chromium treatment and control, two environmental problems remain -- disposal of large quantities of solids which gradually fill the settling ponds and discharge of large quantities of dissolved sodium chloride into surface water. The settled solids can be landfilled and the sodium chloride can be recovered by evaporation techniques and sold.

Sodium Metal

Sodium metal is produced in a Downs Cell Process. Chlorine, produced simultaneously with the sodium, is covered under chlorine. The treatment and control problems for chlorine, once it leaves the cell, are the same for the Downs Cell product as for the mercury and diaphragm cells.

The non-chlorine based wastes consist of brine purification muds, cell wastes such as bricks, graphite, sodium chloride and calcium chloride, and sodium-calcium sludge from the sodium cooling and purification step. Settling ponds may be used for mud removal. Bricks, graphite and other solids may be landfilled. Sodium chloride and calcium chloride may be washed down and allowed to flow to surface water.

In the exemplary plant of this study, the only cell-based wastes not land dumped are the sodium and calcium chlorides. These salts, lost to the extent of an estimated 88 kilograms/kkg of sodium produced, result from cell dumpings, wash tanks, and run offs. These wastes are not currently controlled, and are allowed to run off over the land into surface water. Isolation and collection would make it possible to recover and reuse the sodium and calcium chlorides in the incoming brine system. One possible procedure would be to recycle this weak brine into the brine purification system. This stream can also be concentrated to recover, first any calcium sulfate or sodium sulfate, secondly sodium chloride, and finally, calcium chloride. Sodium chloride and calcium chloride can be dumped. Sodium sulfate can be sold or it may be containerized and disposed of.

Treatment methods for chlor-alkali facilities to eliminate the discharge of process waste water pollutants are applicable to chlorine production using the Downs Cell Process.

Sodium Silicate

Contaminated waste streams containing sodium hydroxide, sodium silicate and filter aids may be sent to settling ponds to remove suspended solids. Waste water may then neutralized and discharged to surface water.

The wastes from sodium silicate plants are minor such that closed loop zero discharge operation is feasible.

Sodium Sulfite

The wastes from this process are primarily sodium sulfite and sodium sulfate. The sulfites constitute a heavy chemical oxygen demand (COD). Typical treatment, at least until recently, has consisted of using large quantities of cooling water to dilute the waste load.

Technology is now being applied to effect a ninety-five percent conversion of sulfite to sulfate by air oxidation.

Recovery of the sodium sulfate from the effluent eliminates process waste is technologically and economically feasible. Recovery eliminates the sulfite process waste and provides both a saleable product and a supply of high quality demineralized water for boiler, cooling tower, or process use.

Sulfuric Acid

There are generally no process wastes from the sulfur-burning sulfuric acid plants. The only water-borne wastes result from spills, leaks, washdowns, and air-borne sulfur dioxide scrubbers.

Leaks, spills and washdowns may be detected by monitoring pH instrumentation. In-process leaks give serious corrosion problems so that shutdown and repair is in order as soon as these leaks are detected. Neutralization with lime or sodium hydroxide is used to control the pH level of the effluent.

Containment, isolation, and reuse or neutralization of minor leaks, spills and washdowns may be obtained with dikes, catch pans, sumps and drain systems. Major storage tanks should be sufficiently diked for complete storage tank capacity containment. Pond linings and pertinent plant grounds coverings of limestone or seashells can provide automatic neutralization. pollution devices to remove sulfur dioxide sometimes contribute to the water-borne waste load. This may be avoided by utilizing sulfur dioxide removal processes which do not generate waste water streams. They should be used for all future installations. These non-water waste processes include double-absorption add-ons (for existing plants), and molecular sieve processes. Several other processes are either in commercial or developmental status.

Existing sulfur dioxide control equipment which invoves water-borne waste can be converted to a waste-free basis by concerntration and recovery of dissolved solids. A sulfuric acid plant in Finland neutralizes its scrubber effluent and concentrates the salt solution for use as fertilizer feed.

Titanium Dioxide

The titanium dioxide industry is in a state of flux. Rutile is in a very short supply and most chloride process producers need this ore or a synthetic version of it. "Synthetic rutiles", or beneficiated low grade ores, are being offered by various foreign and a few domestic suppliers. A company in Japan has operated a 27,000 kkg (24.6 ton) plant since 1971 and is expanding to 40,000 kkg (36.4 tons). One U.S. company has announced a proposed 45,000 kkg/yr (41,000 ton/yr) plant using Australian technology. A comprehensive discussion of ore deposits, their composition, and beneficiation techniques may be found in Dr. Thomas S. Mackey's article "Alteration and Recovery of Ilmenite and Rutile", Australian Mining, November 1972, pp. 18-94.

a) Chloride process

Waste streams for the chloride process fall into two categories:

1. Chlorination wastes composed of sludge from titanium tetrachloride losses and
2. Wastes incurred during the oxidation process and treatment of titanium dioxide product.

Base level treatment usually includes ponding to remove titanium dioxide, ore, coke and other settleable solids.

Three techniques for more effective treatment or disposal of chloride process wastes are available; neutralization of acids and conversion of metallic chlorides to insoluble oxides, ocean barging and deep welling.

A full chemical treatment system is used in plant 009. Chemical neutralization tanks, a clarifier, a thickener, and filters followed by a pond system are used for full acid neutralization, conversion and precipitation of metallic oxides, and concentration of suspended solids into a sludge. The sludge is disposed of as land fill. Both of the main chloride process waste streams, chlorination solids and oxidation process and titanium dioxide product-treatment wastes, are put through the chemical treatment system. The water-borne wastes from the system consist primarily of dissolved calcium chloride.

Deep-welling of the chlorinated wastes is practiced by plant 160. The oxidation and titanium dioxide product treatment wastes are sent through a settling pond system and discharged to surface water. Such deep well disposal is not a general solution to waste abatement practices, since it is not geologically feasible in many sections of the country. Ocean barging is also used to dispose of chloride process wastes, but this method of disposal is not universally applicable either. Both of these disposal techniques are subject to stringent permit requirements and must be consistent with local, State and Federal regulations.

The major chloride process wastes, particularly when low grade ore is used, are ferrous and ferric chlorides. Various proposals have been made for disposing of these chlorides. Included in these proposals are processes for decomposing the iron chlorides to iron oxide and hydrochloric acid (favored for pickle liquor recovery), a process for oxidation of iron chlorides to iron oxides and chlorine, and sale of the iron chlorides as such. Beneficiation of ore by chlorination, separation of iron chlorides, and dechlorination of the iron chlorides is another procedure. All of the above are still in the exploratory, laboratory, pilot plant or other preliminary stage at this time. Bureau of Mines research is already being carried out.

b) Sulfate process

Approximately 2,000 kg of sulfuric acid and 1,000 kg of metallic sulfates/kkg of product are discharged from the sulfate process.

Low grade ores used in the process contribute major quantities of metals which may someday be profitably extracted.

Waste streams generated by the sulfate process include:

(1) sludge from the dissolving step and filtration,
(2) copperas,
(3) strong acid cuts,
(4) weak acid cuts, and
(5) titanium dioxide losses.

Wastes may be collected and sent to a settling pond for suspended solids removal.

Possible treatment and control technologies include filtration and disposal of the sludge from the dissolving step by land dumping, neutralization of both strong and weak acid cuts with limestone, followed by lime treatment to raise the pH to approximately 8 and precipitate iron and other metallic oxides and hydroxides. The conventional chemical treatment system of neutralization tanks, clarifiers, thickeners, filters or centrifuges and ponds may be employed for this purpose.

Ocean barging of the strong acid wastes, sludges and metallic sulfates is now used for disposal by some plants. Uncertainty about the future of this disposal method currently clouds its general application. Also, the weak acid and other wastes are still in many cases being discharged to surface water without significant treatment.

A pilot New Jersey Zinc Company with contract assistance from EPA is investigating the feasibility of acid recovery. Acid recovery is accompanied by treatment of the weak acid, metallic sulfates and titanium dioxide losses in the same type of chemical treatment system as discussed for complete neutralization. Acid recovery reduces the solid waste load inherent with complete neutralization and also decreases the amount of water-borne wastes. Costs are lower for this approach than for complete neutralization.

GENERAL METHODS FOR CONTROL AND TREATMENT PRACTICES IN THE INDUSTRY

Organic content and biological oxygen demands of the effluents for inorganic chemical plants are usually very low. Most alternative control and treatment technologies are well known, established and extensively practiced in the process of producing the inorganic chemicals of this study. Practices such as chemical treatment (neutralization, pH control, precipitation, and chemical reactions), filtration, centrifuging, ion exchange, demineralization, evaporation and drying are all standard unit operations for the industry. Process instrumentation, monitoring and control for the chemical industry is outstanding. Another characteristic of the waste effluents from the inorganic chemical plants of this study is that they differ widely in both chemical nature and amount. Table 39 shows typical water-borne waste loads for the inorganic chemicals included in this study. Soda Ash (Solvay) and titanium dioxide (sulfate process) have raw waste loads in excess of the amounts of chemicals produced. On the other hand, chemicals, such as the mineral acids, calcium carbide and aluminum chloride, generate almost no water-borne wastes. Soda ash (Solvay) wastes are neutral salts while titanium dioxide (sulfate process) wastes are strongly acidic. Therefore, control and treatment technology has to be applied differently for each chemical.

Typical control and treatment technology in use on inorganic waterborne wastes today includes neutralization and pH control on effluent streams, ponds for settling of suspended solids, emergency holding, and storage, and discharge of the neutralized and clarified effluent to surface water.

Discharge of acidic or alkaline wastes to surface water is uncommon. Harmful wastes such as mercury, arsenic, cyanides, chromium and other metals are being removed with increasing efficiency. Technology has been developed for reduction of these harmful materials to very low levels.

Profitable waste segregations and recoveries, closed cycles, leak and spill containments, and in-process waste reductions are demonstrated in the industry. Some of these waste abatement programs have not involved much money, but most have been expensive. Numerous plants have reported program costs ranging from several thousand to several million dollars.

Waste abatement for the inorganic chemicals industry may be accomplished by a variety of methods. These methods may be divided into control and containment practices and treatment techniques. In many cases the control and containment practices are more important than subsequent treatments as far as feasibility and costs of waste treatment are concerned. The reasons for this are discussed in the following sections.

In-process controls

Control of the wastes includes in-process abatement measures, monitoring techniques, safety practices, housekeeping, containment provisions and segregation practices. Each of these categories is discussed including the interactions with treatment techniques.

TABLE 39. Typical Water-Borne Loads for Inorganic Chemicals of this Study

Chemical	Annual Production kkg	Waste Load* kg/kkg Product	Total Waste* kkg/yr
Sodium Chloride	39,000,000	150	5,850,000
Soda Ash (Solvay)	3,630,000	1,500	5,440,000
Titanium Dioxide (Sulfate)	374,000	5,000	1,870,000
Chloride (Non-Rutile)	186,000	400	744,000
Chloride (Rutile)	64,000	75	4,800
Chlorine-Sodium Hydroxide	8,600,000	150	1,300,000
Sodium	150,000	150	22,500
Sulfuric Acid (Sulfur Burning)	27,200,000	0.5	13,600
Sodium Dichromate	136,000	58	13,600
Sodium Silicate	601,000	7.5	4,500
AluminumSulfate	1,020,000	3.5	3,570
Nitric Acid	6,300,000	0.25	1,590
Hydrogen Peroxide	64,000	20	1,270
Hydrofluoric Acid	281,000	4	1,120
Sodium Bicarbonate	186,000	4.5	840
Aluminum Chloride	31,000	24	725
Sodium Sulfite	209,000	3	625
Calcium Carbide	834,000	0.5	415
Hydrochloric Acid (Direct Burning)	200,000	0.5	100

NOTES:

1) Production figures were taken from Chem. & Eng. News, May 7, 1973, pp. 8-9 and "The Economics of Clean Water", Vol. III, Inorganic Chemicals Industry Profile, U.S. Dept. of the Interior, Federal Water Pollution Control Admin., March, 1970.
2) Typical waste loads were estimated from Final Technical Report, Contract No. 68-01-0020, Industrial Waste Study of Inorganic Chemicals, Alkalies and Chlorine, General Technologies Corp., July 23, 1971 (for EPA).
3) Titanium dioxide industry production figures were estimated from Chem. & Eng. News, February 19, 1973, pp. 8-9.

*Solids basis.

Raw Materials

Purity of the raw materials used in the manufacturing process influences the waste load. Inert or unusable components coming into the process are generally discharged as waste.

Control of these impurities can be exercised in many instances. Ores can be washed, purified, separated, beneficiated or otherwise treated to reduce the waste coming into the process. An important facet of this approach is that this treatment can often be done at the mining site where such operations can be contained or handled on the premises. Reduction of shipping charges also favors beneficiation at the mine. Sometimes, as for "synthetic rutile" used in the titanium dioxide chloride process, beneficiated or high quality ore is necessary for developed process technology. Economics of raw material purity need to be balanced against the attendant waste treatment and disposal costs. As waste costs change, it may become more economical to use high quality materials.

Although pure raw materials reduce the inherent waste load, there are instances where, aside from economic factors, it may be desirable to use an impure material. In large manufacturing complexes, wastes from one process may be used for useful purpose in another. This procedure not only eliminates a bothersome waste from one process, it also gives economic value in the other. An example is the use of spent sulfuric acid in decomp plants. Recycled raw materials serve the same desirable function.

Reactions

Except in rare cases such as the mining of salt or soda ash (trona), chemical reaction is involved in the manufacture of inorganic chemicals. Sometimes the reactants are stoichiometrically involved, but more often than not an excess of one or more of the reactants is used. The purposes of the excess vary but include:

1. certainty that the more expensive reactants are completely utilized;
2. yield improvement by driving the reaction in the desired direction;
3. safety concerns where it is imperative that a given reactant be eliminated;
4. shortening reaction time.

Excess reactants must be recovered for recycle or else they become part of the waste load. Often when the cost of the excess reactants was small, it had been more economical to let them go into the waste load rather than recover them. Sodium and calcium chlorides and sulfates are among the most common materials so handled.

Reactions may often be made to operate at more nearly stoichiometric conditions and thereby reduce waste loads. Also, the waste load may be deliberately changed in many cases by changing the reactant ratio. In the burning of hydrogen and chlorine to form hydrogen chloride, operating on the chlorine-rich side provides more troublesome waste than operating on the hydrogen-rich side. Similarly, aluminum chloride made on the chlorine-rich side requires air scrubbing to remove excess chlorine, while the aluminum-rich side does not.

Many chemical reactions are either faster and more complete at high temperatures or are exothermic and generate high temperatures. To produce, control and/or reduce these temperatures, cooling water and steam are often used. If the water or steam is used without contact (such as in a shell and tube heat exchanger), it is not contaminated. If, however, the water or steam contacts the reactants, then contamination of the water results and the waste load increases. Therefore, reaction heating and cooling should be non-contact whenever feasible.

Separations, purifications and recoveries

After reaction, the products, by-products, impurities, inerts and other materials present need to be separated, purified and recovered. Separations are carried out exploiting differences in boiling points, freezing points, solubility and reactivity to separate products from impurities, by-products and wastes. The efficiency of these determines:

1. the fraction of product that is lost as waste or has to be recycled;
2. the purity of the product;
3. control of air pollutants;
4. the recovery and/or disposition of by-products and wastes.

The more complete the separations into recovered product, raw materials that can be recycled, and wastes, the smaller the waste load from the process. The degree of separation actually achieved in the process depends on physical, chemical and economic considerations. These effects will be discussed for the individual chemicals of this study as they apply.

Cooling water and steam are also used in large quantities in the separation and purification steps. The same concepts apply as discussed in the reaction section. Indirect heating and cooling may, in many instances, virtually eliminate waterborne wastes.

Segregation

Probably the most important waste control technique, particularly for subsequent treatment feasibility and economics, is segregation.

Incoming pure water picks up contaminants from various uses and sources including:

1. non-contact cooling water
2. contact cooling water
3. process water
4. washings, leaks and spills
5. incoming water treatments
6. cooling tower blowdowns
7. boiler blowdowns

If wastes from these sources are segregated logically, their treatment and disposal may sometimes be eliminated entirely through use in other processes or recycle. In many instances, the treatment costs, complexity and energy requirements may be significantly reduced. Unfortunately, it is a common practice today to blend small, heavily contaminated streams into large non-contaminated streams such as cooling water effluents. Once this has been allowed to happen, treatment costs, energy requirements for these treatments, and the efficient use of water resources have all been comprised. In general, plant effluents can be segregated into:

1. Non-contaminated cooling water. Except for leaks, noncontact water has no waste pickup. It is usually high volume.
2. Process Water. Usually contaminated but often small volume.
3. Auxiliary Streams. Ion exchange regenerants, cooling tower blowdowns, boiler blowdowns, leaks, washings - low volume but often highly contaminated.

Although situations vary, the basic segregation principle is don't mix large uncontaminated cooling water streams with smaller contaiminated process and auxiliary streams prior to full treatment and/or disposal. It is almost always easier and more economical to treat and dispose of the small volumes of waste effluents - capital costs, energy requirements, and operating costs are all lower. The use of segregation will be discussed for individual chemical processes.

Monitoring techniques

Since the chemical process industry is among the leaders in instrumentation practices and application of analytical techniques to process monitoring and control, there is rarely any problem in finding technology applicable to waste water analysis.

Acidity and alkalinity are detected by pH meters, often installed for continuous monitoring and control.

Dissolved solids concentrations may be estimated by conductivity measurements, suspended solids by turbidity, and specific ions by wet chemistry and calorimetric measurements. Flow meters of numerous varieties are available for measuring flow rates.

The pH meter is the most universal of the in-line monitoring instruments. In acid plants, hydrochloric, sulfuric, phosphoric, nitric, hydrofluoric, and chromic acid leaks in coolers, distillation columns, pumps and other equipment can be picked up almost at once. Spills, washdowns and other contributions also become quickly evident. Alarms set off by sudden pH changes alert the operators and often lead to immediate plant shutdowns or switching effluent to emergency ponds for neutralization and disposal. Use of in-line pH meters will be given additional coverage in the control and treatment sections for specific chemicals.

For monitoring and control of harmful materials such as chromates, batch techniques may be used. Each batch is analyzed before dumping. This approach provides absolute control of all wastes passing through the system. Unless the process is unusually critical, dissolved solids are not monitored continuously. Chemical analyses on grab or composite effluent samples are commonly used to establish total dissolved solids, chlorides, sulfates and other low ion concentrations.

Safety, housekeeping containment

Many of the chemicals of this study or their wastes are either harmful and/or corrosive. Examples are the acids, chromates, chlorine, sodium hydroxide, sodium, and potassium. Mercury from chlor-alkali plants is an example of a harmful waste. Containment and disposal requirements may be divided into several categories:

1. minor product spills and leaks
2. major product spills and leaks
3. upsets and disposal failures
4. rain water runoff
5. pond failures

Minor spills and leaks

There are minor spills and leaks in all industrial inorganic chemical manufacturing operations. Pump seals leak, hoses drip, washdowns of equipment are necessary, pipes and equipment leak, valves drip, tank leaks occur, solids spill and so on. The quantity of waste water as a result of leaks and spills is usually reflected by the company or plant's managerial philosophy relative to housekeeping, washdown and production planning. Leaks and spills represent a potential hazard to workmen in the area of the spill or leak. In some cases the products are valuable (such as hydrofluoric acid and titanium dioxide where every pound lost is like throwing a quarter down the drain). In other cases, where the financial loss may not be as great, personnel safety and equipment corrosion may become paramount. When a leak develops in the heat exchanger of a sulfuric acid plant, the plant shuts down before corrosion gets out of hand. Also, phosphorus is not handled carelessly.

Reduction techniques are mainly good housekeeping and attention to sound engineering and maintenance practices. Pump seals or type of pumps are changed. Valves are selected for minimizing drips. Pipe and equipment leaks are minimized by selection of corrosion-resistant materials.

Containment techniques include drip pans under pumps, valves, critical small tanks or equipment, and known leak and drip areas such as loading or unloading stations. Solids can be cleaned up or washed down. All of these minor leaks and spills should then go to a containment system, catch basin, sump pump or other area that collects and isolates all of them from other water systems. They should go from this system to suitable treatment facilities.

The above mentioned techniques are being used effectively in a number of plants today, and in many cases with enhanced profitability.

Upsets and disposal failures

In many processes there are short term upsets. These may occur during startup, shutdown or during normal operation. Although these upsets represent a very small portion of overall production, they nevertheless contribute to waste loads and must be treated. The upset products may be segregated and possibly reused. In the event that this can not be done, they must be disposed of. Disposal failures require emergency tanks and/or ponds or some other expediency for temporary holding or disposition.

Pond failures

Unlined ponds are the most common treatment facility used by the inorganic chemical industry. Failures of such ponds occur because they are unlined and because they are improperly constructed for containment in times of heavy rainfall.

Unlined ponds may give good effluent control if dug in impervious clay areas or poor control if in porous, sandy soil. The porous ponds will allow effluent to diffuse into the surrounding earth and water streams. This may or may not be detrimental to the area, but it is certainly poor waste control. Lined ponds are the only answer in these circumstances. Many ponds used today are large low-diked basins. In times of heavy rainfall, much of the pond content is released into either the surrounding countryside or, more likely, into the nearest body of water.

Again, whether this discharge is harmful or not depends on the effluent and the surrounding area, but it does represent poor effluent control and may not be permitted by local, State or Federal authorities.

Good effluent control may be gained by a number of methods, including:

1. Pond and diking should be designed to take any anticipated rainfall - smaller and deeper ponds should be used where feasible.
2. Control ponds should be constructed so that drainage from the surrounding area does not inundate the pond and overwhelm it.
3. Substitution of smaller volume (and surfaced) treatment tanks, coagulators or clarifiers can reduce rainfall influx and leakage problems.

Treatment and Disposal Methods

After the in-process control practices discussed in the previous section have been utilized, treatment is usually required for the contaminated streams. In general, these streams may be divided into one of three categories: cooling water, process water, and ancillary water.

Cooling water, either once-through or recycled by means of a cooling tower, should be relatively free of wastes. Any contaminants present would come from leaks (stream to be sent to emergency pond as soon as control monitoring picks it up) or recycle buildups (cooling tower) which are handled as ancillary water blowdowns. In either event, cooling waste contributions are small and treatment, except for incoming water purification, should not normally be needed.

Process and ancillary waterborne wastes do require treatment. The type, degree and costs involved will depend upon specific circumstances unique for each chemical. Various treatment techniques commonly used in the inorganic chemicals manufacturing industry include settling ponds or vessels, filtrations, chemical treatments, centrifugation, evaporation, drying, and carbon adsorption.

Incoming surface water from streams, lakes, or oceans is often filtered to remove suspended objects and solid particles, chemically treated for clarification (small suspended solids particle removal), controlled for pH and chlorinated for BOD control. Ion exchange is used to replace undesirable calcium, magnesium, carbonate and other ions which plate out on boiler, water tower and process equipment as they are concentrated, aerated or subjected to pH changes.

Waste water streams are often subjected to filtrations to remove minor suspended solids. Screens, cloths, cartridges, bags, candles and other mechanisms are used. The driving force may be gravity, pressure or vacuum. Usually the filters are precoated with diatomaceous earth or other filter aids.

Minor chemical treatments on waste water streams include neutralizations for pH control, equalization of streams in a pond or tank to minimize waste composition fluctuations, and chemical reactions or precipitations to remove undesired components.

Settling ponds or vessels are the major mechanism used for reducing the suspended solids content of water waste streams coming from the plant. Their performance and cost depends on the amount of waste involved and the settling characteristics of the solids suspended. In the lower cost category they are small, reflecting either fast settling and/or small, flow rates.

Costs for the above treatments may, in some cases, be derived in the following sections as extrapolations.

Higher cost treatments are rarely needed for incoming water (except in cases where either only very poor quality water is available or very low TDS is required). They are more applicable for treating waste effluents.

Ion Exchange and Demineralizations

Ion exchange and demineralizations are usually restricted in both practice and costs to total dissolved solids levels of 1000 to 4000 mg/l or less. Table 40 gives water compositions as a function of water treatments, including ion exchange and demineralization.

An ion exchanger may be simply defined as an insoluble solid electrolyte which undergoes exchange reactions with the ions in solution. An exchanger is composed of three components: an inert matrix, a polar group carrying a charge and an exchangeable ion carrying an opposite charge. The inert matrix today is usually a cross-linked polymeric resin containing the needed polar groups.

There are two types of ion exchangers: cation and anion. Cation exchangers contain a group such as sulfonic or carboxylic acid. These can react with salts to give products such as the following:

$$RSO_3H + NaCl = RSO_3Na + HCl$$
$$RCO_2H + NaCl = RCO_2Na + HCl$$

TABLE 40. Raw Water and Anticipated Analyses After Treatment

Substance		mg/1 as Ca CO3								
		1	2	3	4	5	6	7	8	9
Cations										
Calcium.	Ca++	100	35	58	1	1	–	–	100	100
Magnesium.	Mg++	100	58	7	1	–	–	–	100	100
Sodium.	Na++	100	100	85	298	164	–	–	100	100
Hydrogen Acidity	H+	0	0	0	C	0	–	–	0	0
Total Cations.		300	198	150	300	165	5	5	300	300
Anions										
Bicarbonate) Alkalinity	HCO3-	150	0	0	150	15	–	–	150	150
Carbonate) Alkalinity	CO3--	0	35	21	0	0	–	–	0	0
Hydroxide) Alkalinity	OH-	0	0	0	0	0	–	–	0	0
Phosphate) Alkalinity	PO4---	0	0	0	0	0	–	–	0	0
Anions										
Chloride	Cl-	75	79	64	75	75	–	–	75	75
Sulfate	SO4--	75	79	63	75	75	–	–	75	75
Nitrate	NO3-	0	0	0	0	0	–	–	0	0
Total Anions.		300	193	150	300	165	5	5	300	300
Total Hardness.		200	93	65	2	1	–	–	200	200
Alkalinity A (Methyl Orange).		150	35	23	150	15	–	–	150	150
Alkalinity B (Phenolphthalein).		0	17	14	0	0	–	–	0	0
Non-Carbonate Hardness.		50	58	55	0	0	–	–	50	50
Sodium Alkalinity.		0	0	0	150	164	–	–	0	0
		mg/1	mg/1	mg/1	mg/1	mg/1	mg/1	mg/1	mg/1	mg/1
Carbon dioxide.	as CO2	30	0	0	30	5-10	5-10	0	30d	30d
Silica.	as SiO2	15	A	5	15	15	15	0.02	15	15
Iron & Manganese.	as Mn & Fe	10	0.2b	0.2b	0.2	0.2	0.2	0.2	0.2c	0.3
Turbidity.		50	0.2b	0.2b	0.2c	0.2c	0.2c	0.2c	0.2c	0.2c
Color.		10	10	10	10	10	10	10	10	10
Total Solids (Cations + SiO2).		315	208	155	315	180	20	5	315	315

(continued on next page)

TABLE 40. Raw Water and Anticipated Analyses After Treatment (cont.)

1. Raw water
2. After cold lime softening and filtration
3. After hot process softening and filtration
4. Ion exchange softening
5. Sodium and hydrogen unit blend and degasification
6. Two-step demineralization (weak anion exchange) and degasification
7. Two-step demineralization (strong base anion resin) and degasification
8. Aeration and filtration
9. Manganese zeolite filters

a. Some reduction will occur
b. Filtered effluent
c. With proper pretreatment
d. Affected by pH adjustment
e. Iron only

Note: Ion exchange processes assume that the water was adequately pretreated.

The above reactions are reversible and can be regenerated with acid.

Anion exchangers use a basic group such as the amino family.

$$\mathrm{RNA_3OH + NaCl \rightarrow RNA_3Cl + NaOH}$$

This is also a reversible reaction and can be regenerated with alkalies. The combination of water treatment with both cation and anion exchangers removes the dissolved solids and is known as demineralization (or deionization). The quality of demineralized water is excellent. Table 41 gives the level of total dissolved solids that is achievable. Membrane and evaporation process water contain significantly higher solids content and need final polishing in a demineralizer if less than 3 mg/l dissolved solids level is required for the application. There are many combinations of ion exchangers which can be used for demineralizations.
Four types of demineralization units will be discussed in the cost analysis development to follow:

1. Fixed bed - strong cation - strong anion
2. Fixed bed - strong cation - weak anion
3. Mixed bed demineralizers
4. Special ion exchange systems.

Special ion exchange systems have been developed for concentrating high dissolved solids content (more than 1000 mg/l total dissolved solids), minimizing regenerant chemicals costs. Some of these special systems are listed in Table 42.

Ion exchange is rarely used to concentrate dissolved solids in waste streams unless some specific ion or ions need to be removed. In fact, usually little overall is gained by this technique since regenerations generate wastes that are often as troublesome to dispose of as the original dissolved materials. Also, the cost of treating waste water with a total dissolved solids concentration of only 1000 mg/l is not low. Demineralization can often be used for concentrating wastes.

Chemical Treatment

Chemical treatments for abatement of water-borne wastes are widespread. Included in this overall category are such important subdivisions as neutralization, pH control, precipitations and segregations, harmful and undesirable waste modification and miscellaneous chemical reactions.

a. Neutralization

Most of the inorganic chemicals of this study are either acidic, alkaline or react with water to give acidic or alkaline

TABLE 41. Water Quality Produced by Various Ion Exchange Systems

Exchanger Setup	Residual Silica mg/l	Residual Electrolytes, mg/l	Specific Resistance ohm-cm @ 25°C
Strong-acid cation + weak-base anion	No silica removal	3	500,000
Strong-acid cation + weak-base anion + strong-base anion	0.01-0.1	3	100,000
Strong-acid cation + weak-base anion + strong-acid cation + strong-base anion	0.01-0.1	0.15-1.5	1,000,000
Mixed bed (strong-acid cation + strong-base anion)	0.01-0.1	0.5	1-2,000,000
Mixed bed + first or second setup above	0.05	0.1	3-12,000,000
Similar setup at immediately above + continuous recirculation	0.01	0.05	18,000,000

TABLE 42. Special Ion Exchange Systems

System I

Application: Feedwater with high solids contents (above 1000 mg/l TDS). There are two variations of this system -- two-bed or threebed setup. Two-bed system consists of weak-base (HCO_3) anion + weak-acid (H) cation exchangers followed by a decarbonator unit. NH_4OH and CO_2 are used to regenerate the anion exchanger and sulfuric acid to regenerate the cation exchanger. In place of decarbonate a second weak-base (OH) anion exchanger is used in the three-bed Desal system.

System advantages: high flow rates; carbon dioxide recovery, good regenerant efficiency. Limitations: solids content of water must be less than 2000 mg/l; highly alkaline feedwater needed for best performance; iron in feedwater cannot be tolerated.

System II

Application: Feedwater with high solids content.

Also employs two- or three-bed setup. Two-bed system consists of strong-acid (H) cation + strong-base (SO_4) anion exchangers followed by decarbonator. Sulfuric acid used to regenerate cation exchanger, raw water the anion exchanger. In three-bed system a weak-acid (H) cation exchanger precedes the strong-acid cation exchanger.

Advantages: raw water can be used to regenerate the strongbase anion exchanger; high quality rinse-water not required. Limitations: ratio of SO_4 to Cl in feedwater must be high; requires high volume of rinse water; low capacity.

System III

Application: Feedwater with high solids content.

Four-bed systems consisting of: strong-base anion (HCO_3) + weak-acid cation (H) + strong-acid cation (H) + weakbase anion (OH) exchangers. $NaHCO_3$ is used to regenerate anion exchangers; sulfuric acid to regenerate cation exchangers.

TABLE 42. Special Ion Exchange Systems (continued)

System III (continued)

Application: (continued)

Advantages: may be used on feedwater containing up to 3000 mg/l solids, content; high capacity and regenerant efficiency. Limitations: number of columns required; low service flow rates; high cost of regenerants.

System IV

Application: Condensate desalination

Mixed-bed ion exchangers have been plagued by the fact that complete resin separation is difficult to achieve -- some cation resin remains mixed with anion resin after backwashing, with the result that sodium is released sooner (lower capacity); some leakage occurs (affecting water quality) since ammonia is usually present in condensate. This is overcome in Ammonex process by regenerating cation exchanger with acid and first regenerating anion exchanger with caustic and then with ammonia to remove the sodium present in anion exchanger.

System V

Application: Condensate desalination

Water quality and run length improved similarly as in Ammonex process except that anion exchanger is regenerated with caustic and lime rather than caustic and ammonia.

System VI

Application: Condensate desalination

Water quality and run length improved by separating mixedbed with strong caustic solution then regenerating beds in customary procedure; i.e., with acid for cation exchanger and caustic for anion exchanger.

solutions. Others have production wastes or byproducts of acidic or basic nature. Before disposal in surface water or other medium this acidity or alkalinity needs to be reduced and controlled. The most common method is to treat acidic streams with alkaline materials such as limestone, soda ash, sodium hydroxide, and lime. Alkaline streams are treated with acids such as sulfuric. Whenever possible, advantage is taken of the availability of acidic waste streams to neutralize basic waste streams and vice versa.

b. pH Control

The control of pH may be equivalent to neutralization if the pH is adjusted to approximately 7.0. As discussed in the earlier control section, control of excess acidity or alkalinity is best accomplished by pH meter monitoring. The usual acceptable range for pH control is 6.0-9.0 for discharge water.

c. Precipitations and Segregations

The reaction of two soluble chemicals to produce insoluble or precipitated products is the basis for removing many undesired waterborne (and airborne) wastes. The use of this technique varies from lime treatments to precipitate common sulfates, fluorides and carbonates, to sodium sulfide precipitations of mercury, copper, lead and other harmful metals.

d. Modifications

Chemical reactions can also be used to change or destroy undesirable wastes. Among the more common are the oxidation-reduction mechanisms. Cyanides can be oxidized to cyanates; hexavalent chromium reduced to the trivalent form; hypochlorites changed to chlorides; sulfites oxidized to sulfates. These examples and many others are basic to the modification of inorganic chemicals waterborne wastes to make them less troublesome.

Settling Ponds and Vessels

Many chemical treatments produce suspended solids which need to be removed from the waste streams. In the moving, agitated, often turbulent waste streams flowing through pipes, tanks, and channels, there is little opportunity to do this. In fact, it would usually be undesirable to do so in any event -- pipes and flow channels are not easy or economical to clean.

To facilitate settling of suspended solids, large quiet settling ponds and vessels are needed. Settling ponds are the foremost industrial treatment for removing suspended solids.

The size and number of settling ponds differ widely depending on the settling functions required. Waste streams with small suspended solids loads and fast settling characteristics require one or two small ponds with a surface area of less than 0.1-0.2 ha (0.25-0.5 ac). Other waste streams with heavier suspended solids loads and/or slower settling rates may require five to ten ponds and up to 405 ha (1000 ac) total surface area.

Although not as common as settling ponds, tanks and vessels are employed for reduction of suspended solids loads in inorganic chemical production waste streams. Commercially these units are listed as clarifiers or thickeners depending on whether they are light or heavy duty. They also have internal baffles, compartments, sweeps and other directing and segregating mechanisms to provide more efficient performance. This feature, plus the positive containment and control and reduced rainfall influence (smaller area compared to ponds), should lead to increasing use of vessels and tanks in the future.

Filtration (Major)

Major filtration equipment includes pressure and vacuum units of various designs, including plate-and-frame leaf and rotary constructions. Although it is entirely feasible for filtration equipment to be used for removing suspended solids from waste streams, most are not filtered. The preferred treatment for removing suspended solids is settling ponds. Filtrations are common for collection of solid wastes from harmful chemical treatments where complete removal is imperative. Sludges containing metal sulfides (mercury, arsenic, etc.) are good examples of materials handled in this way.

Centrifuging

When the force of gravity is not sufficient to separate solids and liquids to the desired degree, or in the desired time, more powerful centrifugal force can be utilized. Although there are many types of centrifuges, most industrial units can be broken down into two major categories -- solid bowl and perforated bowl. The solid bowl centrifuge, as its name indicates, consists of a rapidly rotating bowl into which the stream with suspended solids is introduced. Centrifugal action of the spinning bowl separates the solids from the liquid phase and the two are removed separately.

The perforated bowl centrifuge has holes in the bowl through which the filtrate escapes by centrifugal force. The solids are retained on the filter inside the bowl and removed either continuously (such as for the pusher types) or in batch fashion.

Centrifuges are not widely used for inorganic chemical waste streams, since it is rare that settling ponds or filters are not adequate for the same suspended solids removal job.

Carbon Adsorption

On the rare occasions that inorganic chemicals waste streams contain organic materials, one of the appropriate treatments to remove these organic components is carbon adsorption. When waste streams containing organic contaminants are passed through activated carbon beds, the organic material is adsorbed. When the carbon bed is saturated with this organic substance, the bed may be regenerated by burning off the adsorbed organic and returning the carbon to service.

Reverse Osmosis

The small pore size of the reverse osmosis membrane is both its strength and its weakness. Its strength comes from the molecular separations that it can achieve. However, it is susceptible to blinding, plugging, and chemical attack. Acidity, suspended solids, precipitations, coatings, dirt, organics and other substances can make it inoperative. Membrane life is critical and difficult to predict in many cases. Because of these restrictions its industrial applications are few. Fortunately, the inorganic chemistry industry water purification needs are similar to those of the areas where reverse osmosis has been shown to be applicable -- treatment of brackish water and low (500-20,000 mg/l) dissolved solids removal. Organics are usually absent, suspended solids are low or can be made low rather easily, acidity is easily adjusted, and most of the dissolved solids are similar to those in brackish water -- sodium chlorides, sulfates and their calcium counterparts.

The reverse osmosis membranes used commercially are generally one of two types -- flat sheet or hollow fiber. For maximum membrane area in the smallest space, various sheet configurations have been devised including tubes, spiral winding, and sandwich-type structures. Sheet membranes have been largely cellulose acetate, while hollow fibers have been largely polyamides. Costs for different membrane configurations are roughly comparable. The type selected depends upon the specific application.

Regardless of membrane type or material, the basic unit of construction is the module (or package of membrane materials). The module is usually integral and of the plug-in type, where a faulty module can be easily (but not inexpensively) replaced. The modules are the heart of the reverse osmosis process, with ancillary equipment such as pumps, tanks, piping, pretreatment facilities and other hardware performing peripheral functions. Module cost alone comprises one-third to one-half of the installed capital investment.

Detailed cost figures, both capital and operating, are given in Section VIII.

Evaporation Processes

Evaporation is the only method of general usefulness for the separation and recovery of dissolved solids in water. Other processes either involve mere concentration (reverse osmosis) or introduce contaminations for subsequent operations (demineralizer regenerants and chemical precipitations).

The evaporation process is well known and well established in the inorganic chemical industry. Separations, product purifications, solution concentrations are commonly accomplished by evaporative techniques. In-depth technology for handling the common dissolved solids in water waste streams has been developed in the soda ash, salt, calcium chloride, and sea water chemical industries. In addition, numerous desalination plants producing fresh water from brackish or sea water are scattered all over the world and have been in operation for a number of years. Seawater generally has approximately 35,000 mg/l dissolved solids (3.5 percent by weight) while brackish water has 2,000 to 25,000 mg/l depending on location.

Evaporation is a relatively expensive operation. To evaporate one kg of water, approximately 550 kg-calories of energy is required and the capital cost for the evaporating equipment is not low. For these reasons industrial use of evaporation in treating waste water has been minimal. As the cost of pure water has increased in portions of the United States and the world, however, it has become increasingly attractive to follow this approach.

The treatment of water waste streams by evaporation almost always has utilized the principle of multi-effects to reduce the amount of steam or energy required. Thus, the theoretical difficulty of carrying out the separation of a solute from its solvent is the minimum amount of work necessary to effect the particular change, that is the free energy change involved. A process can be made to operate with a real energy consumption not greatly exceeding this value. The greater the concentration of soluble salts, the greater is the free energy change for separation, but even for concentrated solutions the value is much lower than the 550 kg-cal/kg value to evaporate water. Multi-effect evaporators use the heat content of the evaporated vapor stream from each preceding stage to efficiently (at low temperature difference) evaporate more vapor at the succeeding stages. Thus the work available is used in a nearly reversible manner, and low energy requirement results. However, a large capital investment in heat transfer surface and pumps is required. The interaction of the capital equipment costs versus energy or operating costs will be discussed in detail in the treatment costs section.

Drying

After evaporative techniques have concentrated the dissolved solids to high levels, the residual water content must usually be removed before recovery, sale or disposal. Water content will range from virtually zero up to 90 percent by weight. Gas- or oil-fired dryers, steam-heated drum dryers or other final moisture-removing equipment can be used for this purpose. Since this drying operation is a common one in the production of inorganic chemicals themselves, technology is well known and developed. Costs are mainly those for fuel or steam.

Disposal Practices

Disposal of the waterborne wastes from inorganic chemicals manufacturing represents the final control exercised by the waste producer. A number of options are available. They include discharge to surface water -- river, lake, bay or ocean -- and where safe and permitted, land disposal by running the effluent out on land and letting it soak in or evaporate. Wastes may be disposed of into an industrial waste treatment plant. Treatment and reuse of the waste stream can also be practiced. In dry climates unlined evaporation ponds, if allowed, could be used.

Higher-cost disposal systems include lined evaporation ponds, deep well disposal, and high-cost treatment prior to disposal or recovery. Such methods are used for wastes which cannot be disposed of otherwise. These wastes contain strong acids or alkalies, harmful substances, or large quantities of dissolved solids.

Feasibility, use, and cost figures can be discussed for:

1. unlined evaporation ponds
2. lined evaporation ponds
3. deep wells

Unlined Evaporation Ponds

Two requirements must be met for an unlined evaporation pond to be successfully utilized. First, it must be located in an area in which unlined ponds are allowed, and secondly, the rainfall in that area must not exceed the evaporation rate. This second requirement eliminates most of the heavily industrialized area. For the low rainfall areas, evaporation ponds are feasible with definite restrictions. Ponds must be large in area for surface exposure. Evaporation of large amounts of waste water requires large ponds. The availability and costs of sufficient land place another possible restriction on this approach.

Lined Evaporation Ponds

The lined evaporation ponds now required in some sections of the country have the same characteristics as developed for the unlined ponds -- large acreage requirements and a favorable evaporation-rainfall balance. They are significantly higher in cost than an unlined pond. Such costs are developed in Section VIII. Reduction of the evaporation load is a significant advantage. For this reason, plus the short supply and high cost of water in much of southwestern United States, distillation and membrane processes are beginning to be used in these regions.

Deep Wells

Deep well disposal can only be used under special conditions consistent with State and Federal regulations. While used for brine disposal in the petroleum and salt industries, deep wells are usually reserved for wastes such as strong acids, chromates, pickle liquor, and corrosive metallic salt solutions for which no other disposal system is available or environmentally acceptable. Deep well disposal should be considered only a temporary expedient until suitable recovery, reuse, or treatment methods are developed and demonstrated to be practical.

There are several reasons for this specialization, including:

1. Costs - A single well costs up to $1,500,000 depending on depth, drilling ease and criticalness, casing, exploration and monitoring involved.

2. Geological - The geological structure in the area is of utmost importance. In many parts of the country, deep wells are not possible. Even in those sections where the geological structure permits their use, deep wells must be carefully planned and coordinated using the best geological information and expertise available.

3. Drilling Considerations - Deep wells are drilled by specialists using oil well technology. While this technology is well developed, there is always the possibility that something expensive will go wrong -- cracks, lost drills, impermeable formations, etc.

4. Reliability - Deep wells often plug or develop operating difficulties even after several years of good performance.

5. Extensive Pretreatment may be necessary to remove organics, suspended solids and other undesirable waste components.

6. The risk of contamination of underground potable water or seismic effects.

Most wells are approximately the same size and range in flow rate from 12.6-56.8 l/sec with the average being about 18.9-25.2 l/sec. This corresponds to approximately 1890 cu m/day capacity.

SECTION VIII

COST, ENERGY AND NON-WATER QUALITY ASPECTS COST AND REDUCTION BENEFITS OF TREATMENT AND CONTROL TECHNOLOGIES

The inorganic chemical industry has large energy requirements for gas furnaces, kilns, calciners, electric furnaces, reactors, distillation columns, and evaporators and other common equipment. In contrast, treatment practices consume less than one tenth of one percent of this amount. Chemical reactions and pond settling, the most commonly used treatments, required almost no energy. Filtrations, centrifuging, and other separation techniques are still relatively low energy processes. The only two high energy treatments, evaporation and drying, are now rarely used. Utilizing these treatment techniques to the extent covered in the cost effectiveness discussions later in this section will still maintain treatment energy at a tiny fraction of the total energy for the industry. Table 43 summarizes cost and energy requirements for the manufacture of the inorganic chemicals of this report. To bring the processes to zero waterborne waste effluent through total recycle of process water, rough estimates for additional capital expenditures are 295 million dollars. Of this amount, three industries contribute almost eighty percent. These industries -- soda ash (Solvay Process), chlor-alkali, and titanium dioxide -- have vastly different situations from the other chemicals.

Titanium dioxide has no satisfactory replacement. It can absorb and pass on the large capital and operating costs needed for waterborne waste cleanup. This major clean-up is also long overdue. Development and application of existing treatment technology can save the titanium dioxide industry an estimated 100 million dollars over the full neutralization costs given in Table 43.

The chlor-alkali industry differs from both soda ash (Solvay) and titanium dioxide in that mainly in-process changes and more efficient use of raw materials are required to attain zero waterborne waste. There are many ways to accomplish this, some of which are suggested in Sections VII and VIII of this report.

Other industries that have major capital expenditures in Table 43, sulfuric acid, nitric acid, sodium metal (which is similar in process wastes to chlor-alkali plants), aluminum sulfate, sodium dichromate, and sodium chloride (brine or mining) have these costs primarily because of the large size of the industry or harmful wastes. Except for sodium chloride (brine or mining) and sodium dichromate, all waste abatement costs for these chemicals are below 1.5 percent of the list price.

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TABLE 43. Summary of Cost and Energy Information for Attainment of Zero Discharge

Chemical	Additional Capital, $	Additional Energy 10^6 Btu/yr	Additional Energy 10^6 Kg cal/yr	Incremental Cost $/ton	Incremental Cost $/metric ton	Percent of List Price	June, 1973 List Price $/ton	June, 1973 List Price $/metric ton
Aluminum Chloride	0	0	0	0	0	0	>255	280
Aluminum Sulfate	4,700,000	17,000	4300	0.90	1.0	1.4	62.80	69
Calcium Carbide	0	0	0	0	0	0	171.40	188
Hydrochloric Acid	250,000	0	0	0.05	0.06	0.04	110(100%)	121
Hydrofluoric Acid	1,180,000	3300	8350	13-16	14-18	2.5	560(100%)	617
Lime	0	0	0	0	0	0	19.50-21.75	21.50-24
Nitric Acid	11,000,000	0	0	0.22	0.24	0.18	113(100%)	124
Patassium Metal	0	0	0	0	0	0	--	--
Potassium Chromates	90,000	210	53	4.65	5.15	0.97	480	528
Sodium Bicarbonate	0	0	0	0	0	0	88	97
Potassium Sulfate	1,570,000	680,000	162,000	1.60	1.16	3.7	42.50	47.50
Sodium Chloride (Solar)	0	0	0	2.20	2.42	25.9-11.0	8.50-20	9.40-22
Sodium Silicate	850,000	332,000	84,000	0.90	1.0	0.95	95	102
Sulfuric Acid	20,000,000	0	0	0.10	0.11	.33	28-32	30.75-35
Hydrogen Peroxide (Organic)	350,000	0	0	1.00	1.10	0.2	460 (70%Sol'n)	505
Sodium Metal	4,700,000	0	0	2.25	2.48	0.6	375	412
Sodium Sulfite	3,730,000	116,000	29,300	2.50	2.75	2.1	117	129
Calcium Chloride	1,040,000	0	0	0.20	0.22	0.5	42	46
Sodium Chloride (brine)	7,750,000	0	0	1.00	1.10	7.15-4.16	14-24	15.40-26.45
Chlor-Alkali	40,000,000	800,000	202,000	0.50 (combined product basis)	0.45	~0.5	Cl_2 $75 NaOH $110 (75%)	$83 $121
Hydorgen Peroxide (Electrolytic)	15,000	870	220	0.25-.75	0.27-.83	0.1	460 (70%Sol'n)	507

(continued on next page)

TABLE 43. Summary of Cost and Energy Information For Attainment of Zero Discharge (continued)

Chemical	Additional Capital, $	Additional Energy 10^6 Btu/yr	10^6 kg cal/yr	Incremental Cost $/ton	$/metric ton	Percent of List Price	June, 1973 List Price $/ton	$/metric ton
Sodium Dichromate	4,100,000	240,000	60,700	16	18	4.6	345	380
Sodium Sulfate	0	0	0	0	0	0	24-33	26-36
Soda Ash	*****25,000,000	200,000	50,200	1.60	1.76	4.5	35.50	39
Titanium Dioxide (Chloride)	****74,000,000	675,000	170,000	64	70	11.4	550-570	605-615
Titanium Dioxide (Sulfate)	96,000,000	535,000	135,000	96	103	17.1	550-570	605-615
Totals	294,895,000	3,590,000	905,000	--	--	--	--	--

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*Chemical Marketing Reporter, June 4, 1973.

**Based on 3 million tons/year vacuum pan salt production from Salt, Bureau of Mines Minerals Yearbook, 1969.

***Based on $2.00/ton chlor-alkali production -- estimated from cost effectiveness data in Section VIII

****Based on full neutralization plus demineralization costs as given in Section VIII

*****Based on deep-welling costs as in section VIII

For all chemicals except soda ash, titanium dioxide, sodium dichromate, and sodium chloride (solar), the yearly cost for total water-borne waste abatement is less than 4 percent of the current list price.

Energy requirements of 9.05 x 10^{11} kg cal/yr (3.6 X 10^{12} BTU/yr) or the energy equivalent to burning 10,220 cu m (3.6 million gal) of fuel oil for the elimination of water-borne wastes for the chemicals of this study are less than that currently consumed by one large Solvay soda ash plant.

Thermal pollution was not encountered in this study nor was noise or other types of pollutions.

In general, plant size itself does not appear to be a significant factor influencing waste effluents on a kkg waste/kkg of product basis. Multichemical complexes have an advantage over single isolated facilities on costs and options for waste utilization. Plant age does have some influence, with the new plants, naturally, being favored. These are by no means the controlling criteria, however. For example, nineteen exemplary plants used in the cost effectiveness development given later in this section have an average age of 21 years, with five plants of 30 years or greater age and six of 10 years or less age.

Geographical location is often a critical factor for waste disposal costs. Availability of deep welling, ocean barging, or solar evaporation options is an advantage. Also, the western United States has more incentive to recover and reuse ocean water than the east.

New plants being built can avoid major future waste abatement costs by inclusion of:

(1) Dikes, emergency holding ponds, catch basins, and other containment facilities for leaks, spills and washdowns.
(2) Piping, trenches, sewer, sumps and other isolation facilities to keep leaks, spills and process water separate from cooling and sanitary water.
(3) Non-contact condensers for cooling water. Barometric condensers should be avoided.
(4) A full water treatment system, including demineralization, reverse osmosis, evaporative and solids waste handling equipment when needed.
(5) Efficient reuse, recycling and recovery of all possible raw materials and by-products regardless of inherent value. Sodium chloride and sodium sulfate are two by-products which frequently cause trouble.
(6) Closed cycle water utilization whenever possible. Closed cycle operation eliminates all water-borne wastes. Generally, if water is pure enough for discharge, it is pure enough for reuse.

Cost References and Rationales

Cost information contained in this report was obtained directly from industry during exemplary plant visits, from engineering firms and equipment suppliers, and from the literature. The information obtained from these latter three sources has been used to develop general capital, operating and overall costs for each treatment and control method. Costs have been put on a consistent industrial calculation basis of ten year straight line depreciation plus allowance for interest at six percent per year (pollution abatement tax-free money) and inclusion of allowance for insurance and taxes for an overall fixed cost amortization of fifteen percent per year. This generalized cost data plus the specific information obtained from plant visits was then used for the cost effectiveness estimates in this section and whenever else costs are mentioned in this report.

Cost developments, calculations, references and rationale for treatment and disposal techniques pertinent to the inorganic chemicals industry are detailed in Supplement A. In addition to the costs developed in Supplement A, costs for specific plant treatment systems are given in Supplement B. The combination of these two costs sources and engineering judgment extrapolations from them are used for cost effectiveness development.

Definition of Levels of Control and Treatment

Using the general models as given in Figures 62 and 63, cost and energy effectiveness values for each chemical subcategory have been developed. Four levels of treatment and control are considered:

Level A -- Base level practices followed by most of the industry and exceeded by exemplary plants.

Level B -- Treatment and control practices at the average exemplary plant.

Level C -- Based upon the best technically and economically feasible treatment and control technology.

Level D -- Complete water-borne waste elimination. This level may or may not be economically feasible for the specific chemical.

Aluminum Chloride

No water-borne process wastes are generated in the manufacture of aluminum chloride. The only ancillary waste stream results from wet air pollution control devices. Two exemplary plants have no wastes from this source. Plant 125 has been chosen for cost effectiveness development (see Table 44). This is a 30 year old

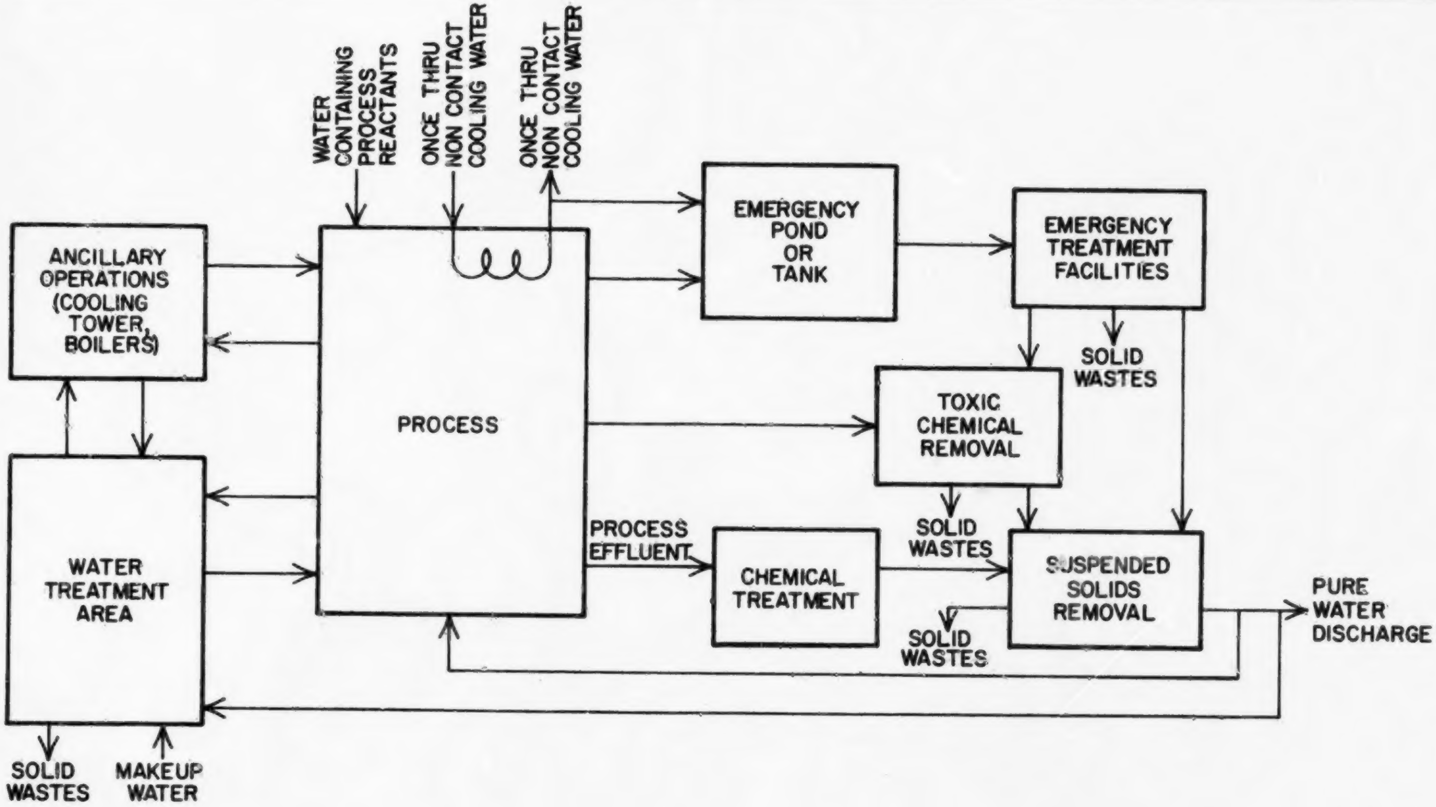
WATER CONTAINING PROCESS REACTANTS
ONCE THRU NON CONTACT COOLING WATER
ONCE THRU NON CONTACT COOLING WATER
ANCILLARY OPERATIONS (COOLING TOWER, BOILERS)
PROCESS
EMERGENCY POND OR TANK
EMERGENCY TREATMENT FACILITIES
SOLID WASTES
TOXIC CHEMICAL REMOVAL
SOLID WASTES
PROCESS EFFLUENT
CHEMICAL TREATMENT
SUSPENDED SOLIDS REMOVAL
SOLID WASTES
PURE WATER DISCHARGE
WATER TREATMENT AREA
SOLID WASTES
MAKEUP WATER

FIGURE 62
MODEL FOR WATER TREATMENT AND CONTROL SYSTEM
INORGANIC CHEMICALS INDUSTRY

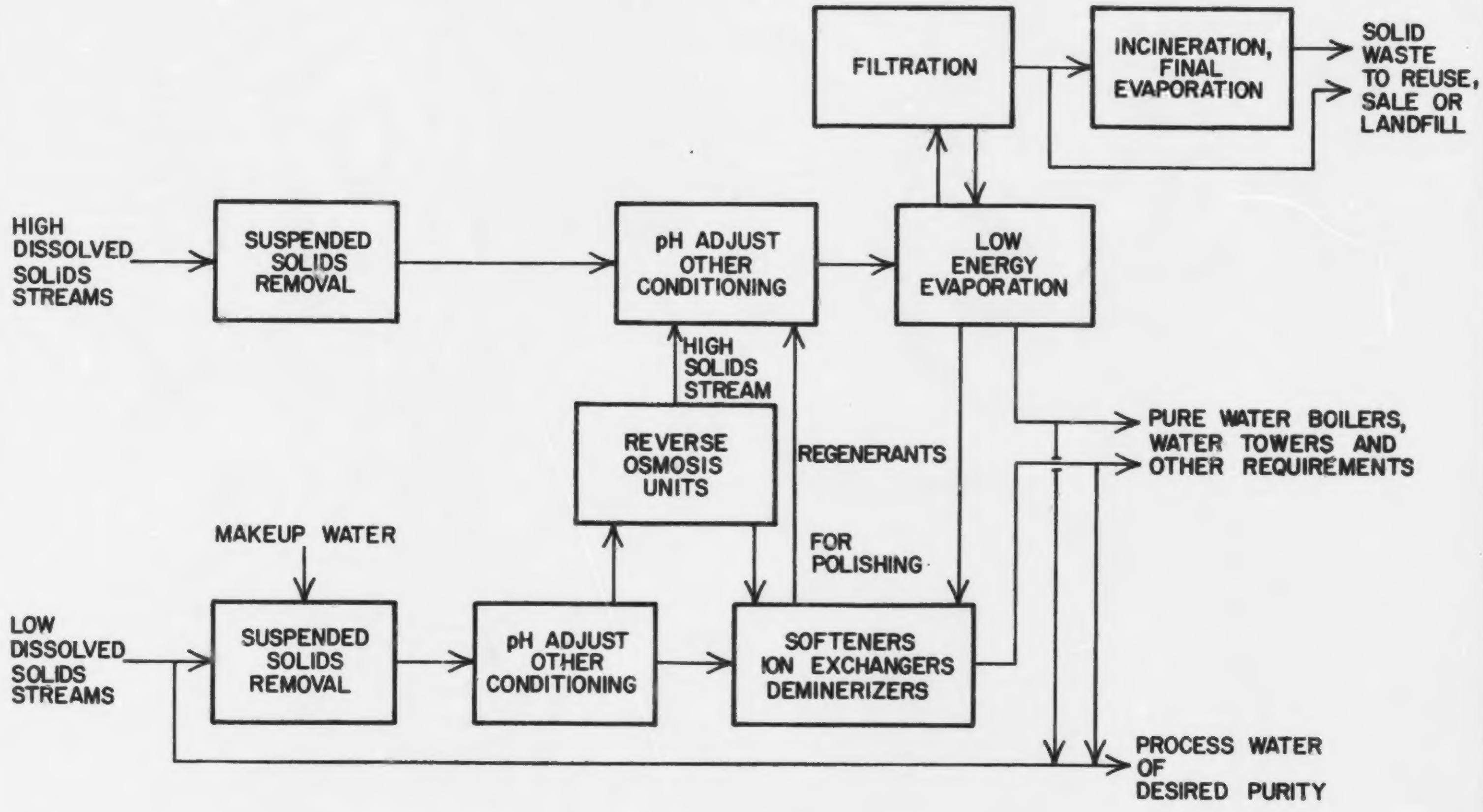
HIGH DISSOLVED SOLIDS STREAMS
SUSPENDED SOLIDS REMOVAL
pH ADJUST OTHER CONDITIONING
LOW ENERGY EVAPORATION
FILTRATION
INCINERATION, FINAL EVAPORATION
SOLID WASTE TO REUSE, SALE OR LANDFILL
HIGH SOLIDS STREAM
REVERSE OSMOSIS UNITS
REGENERANTS
FOR POLISHING
MAKEUP WATER
LOW DISSOLVED SOLIDS STREAMS
SUSPENDED SOLIDS REMOVAL
pH ADJUST OTHER CONDITIONING
SOFTENERS ION EXCHANGERS DEMINERIZERS
PURE WATER BOILERS, WATER TOWERS AND OTHER REQUIREMENTS
PROCESS WATER OF DESIRED PURITY

FIGURE 63
MODEL FOR WATER TREATMENT SYSTEM
INORGANIC CHEMICALS INDUSTRY

TABLE 44

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: Aluminum Chloride (22.5 kkg/day (25 tons/day) Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	25,000	100,000	100,000	100,000
Annual Costs:				
Interest + Taxes and Insurance	1250	5,000	5,000	5,000
Depreciation	2500	10,000	10,000	10,000
Operating and Maintenance Costs (excluding energy and power costs)	2000	0**	0**	0**
Energy and Power Costs	3500	~0	~0	~0
Total Annual Cost	9250	15,000***	15,000***	15,000***

Effluent Quality:

Effluent Constituents Parameters (Units) (kg/kkg (lbs/ton))	Raw Waste Load	Resulting Effluent Levels		
Aluminum Chloride + Chlorine (Airborne)	75(150)*	75(150)*	--------2.5 (5)****------	

Level A - evaporation and reuse
Level B - recycle of scrubber water

---

*Residual air-borne wastes (where scrubbers are used for air pollution abatement this is water-borne).

**Operating costs of $18,000/yr balanced by sale of product as aqueous aluminum chloride solution.

***Credited to air pollution control water pollution control cost is zero.

****Air-borne waste passing scrubber, scrubber liquor sold or recycled.

plant of nominal 22.5 kkg/day (25 ton/day) capacity. Treatment facilities have been recently installed.

Energy requirements are low (small pumps and stirrers) and are estimated to be 0.75 kwhr (1 hp-hr). Converting this to common units gives 5.3 x 10^6 kg cal (2.1 x 10^7 BTU).

For the entire industry, the energy requirement would be 1.7 x 10^7 kg cal (6.8 x 10^7 BTU).

Treatment costs for air pollution control are $1.88/kkg ($1.70/ton) of product. Treatment costs and energy requirements for water pollution control are zero.

Aluminum Sulfate

Two exemplary closed-cycle plants, 049 and 063, were studied. Plant 063 is chosen for cost effectiveness analysis. This 46 year old plant has an average production of 36 kkg/day (40 tons/day). Cost effectiveness information is given in Table 45.

Energy requirements for pumps, clarifiers, drives, etc., are approximately 7.5 kwhr (10 hp-hr). Annual requirements are 5.3 x 10^7 kg cal (2.10 x 10^8 BTU).

Entire industry energy for treatment is estimated as 4.3 x 10^9 kg cal (1.7 x 10^{10} BTU).

Costs for closed cycle zero effluent operation are $1.87/ kkg ($1.70/ton) of which $1.00/kkg ($0.90/ton) of product represents additional cost above typical operation in all plants.

Calcium Carbide

The calcium carbide manufacturing process generates no water borne waste. The only possible contributions result from wet air pollution control devices used to remove dusts and particulates from the gas streams. Costs for treating air pollution abatement contributions to water effluents are credited to air pollution costs. Therefore, energy and costs for waste water treatment for calcium carbide are zero.

For information purposes, a cost-effectiveness sheet, Table 46, has been prepared showing air pollution abatement costs for plant 190. In this case air pollution control costs are zero since recovered raw materials pay for total annual costs.

Calcium Oxide and Calcium Hydroxide

There is no water-borne waste from the process. Therefore, no cost or energy is involved.

TABLE 45.

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: Aluminum Sulfate (36 kkg/day (40 tons/day) Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	40,000	100,000		
Annual Costs:				
Interest + Taxes and Insurance	2,000	5,000		
Depreciation	4,000	10,000		
Operating and Maintenance Costs (excluding energy and power costs)	5,000	8,000		
Energy and Power Costs	--	1,000		
Total Annual Cost	11,000	24,000		

Effluent Quality:

Effluent Constituents Parameters (Units) kg/kkg (lbs/ton)	Raw Waste Load	Resulting Effluent Levels	
Silicon Dioxide	20 (40)	1 (2)	------------0-----------
Titanium Dioxide	20 (40)	1 (2)	------------0-----------
Aluminum Oxide	10 (20)	1 (2)	------------0-----------
Aluminum Sulfate	0.25 (0.5)	0.05 (0.1)	------------0-----------

A -- Typical treatment taken as pond settling -- total pond area of 0.4 hectare (one acre) (unlined).

B -- Best average treatment level involves clarifiers plus additional ponds + level A ponds and closed cycle operation.

TABLE 46.

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: **Calcium Carbide (127 kkg/day (140 tons/day) Capacity)**

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	0	Not known		
Annual Costs:				
Interest + Taxes and Insurance		Not known		
Depreciation		Not known		
Operating and Maintenance Costs (excluding energy and power costs)	0	Not known		
Energy and Power Costs	0	Not known		
Total Annual Cost	0	0	0	0

Effluent Quality:

Effluent Constituents Parameters (Units) Kg/kg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Coke Dust	50(100)	50(100)	0	0	0
Furnace Dust	85(170)	85(170)	0	0	0
Packing Dust	10(20)	10(20)	0	0	0

Level A -- In many plants there are no dust collectors.

Level B -- Plant 190 installations are expected to pay for themselves in recovered raw material value. Therefore, annual air pollution control cost is zero.

For informational purposes cost effectiveness Table 47 is given for eliminating air pollution. Cost is $1.45/kkg ($1.32/ton) for dry bag collection installations. If water scrubbing plus elimination of water-borne wastes is more economical than $1.45/kkg ($1.32/ton) of product, then water scrubbing and reuse may be used.

Calcium Chloride

Calcium chloride comes from two major sources, Solvay soda ash by-product and brine chemicals by-product. A 45 year old, 450 kkg/day (500 ton/day) brine reclamation plant, 185, is used for cost effectiveness development, as shown in Table 48.

Cost for elimination of present wastes is roughly estimated as $0.22/kkg ($0.20/ton) of product.

No additional energy requirements are involved.

Chlorine and Potassium or Sodium Hydroxide

a) Mercury cell process

Both chlorine and sodium hydroxide are produced by the mercury cell process. Potassium hydroxide is produced similarly by starting with potassium chloride brine instead of sodium chloride.

Cost effectiveness values are developed in Table 49 using two year-old 158 kkg/day (175 ton/day) (chlorine basis) plant 098.

For zero water-borne wastes the cost above Levels A and B mercury removal is approximately $1.00/kkg($0.90/ton) of chlorine produced. Spreading these costs to chlorine and sodium hydroxide co-products reduces the value to approximately $0.55/kkg ($0.50/ton) of products.

Roughly 2.52×10^9 kg cal/yr (1.0×10^{10} BTU/yr) additional energy is required for this plant.

Plants have now reduced water effluent mercury discharges to approximately 0.045-0.225 kg/day (0.1-0.5 lb/day) by spending Level A and B money. Some exemplary plants have spent Level C money (plant 098 is at this level).

b) Diaphragm cell process

Diaphragm cells also produce both chlorine and sodium hydroxide (or potassium hydroxide if potassium chloride brine is used).

Table 50 gives the progressive cost effectiveness development for one year old 2070 kkg/day (2300 ton/day) plant 057. Costs for

TABLE 47

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: Lime - Air Pollution Costs Only (281 kkg/day (310 tons/day) Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	0	675,000	675,000	675,000
Annual Costs:				
Interest + Taxes and Insurance	0	33,750	33,750	33,750
Depreciation	0	67,500	67,500	67,500
Operating and Maintenance Costs (excluding energy and power costs)	0	35,000	35,000	35,000
Energy and Power Costs	0	2,500	2,500	2,500
Total Annual Cost	0	138,750	138,750	138,750

Effluent Quality:

Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Kiln Dusts	67(134)	67(134)	~0	~0	~0

Level B -- Dry bag collectors installed.

TABLE 48.

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: **Calcium Chloride (450 kkg/day (500 tons/day) Capacity)**

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A*	B	C	D
Investment	0	200,000	200,000	200,000
Annual Costs:				
Interest + Taxes and Insurance	0	10,000	10,000	10,000
Depreciation	0	20,000	20,000	20,000
Operating and Maintenance Costs (excluding energy and power costs)	0	0	0	0
Energy and Power Costs	0	0	0	0
Total Annual Cost	0	30,000	30,000	30,000

Effluent Quality:

Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Calcium Chloride	30(60)	30(60)	0.5(1)	~0	~0
Sodium Chloride	0.5(1)	0.5(1)	0	~0	~0
Ammonia	0.5(1)	0.5(1)	0	~0	~0

Level A -- Normally these wastes, as dissolved solids are discharged to surface water in non-exemplary of soda ash plants.
Level B -- Replacement of barometric condensers with non-contact heat exchangers.
Level C -- Elimination of packing station water-waste contributions.

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*Level A corresponds to present performance of "exemplary" plant in this table. Level B modelled to near future plans of this plant.

TABLE 49

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: **Mercury Cell Chlor-Alkali (158 kkg/day (175 tons/day) Capacity)**

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	500,000	500,000	700,000	750,000
Annual Costs:				
Interest + Taxes and Insurance	25,000	25,000	35,000	37,500
Depreciation	50,000	50,000	70,000	75,000
Operating and Maintenance Costs (excluding energy and power costs)	55,000	55,000	61,000	64,000
Energy and Power Costs	1,000	1,000	2,000	7,000
Total Annual Cost	131,000	131,000	168,000	183,500

Effluent Quality:

Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Sodium Chloride	50(100)	50(100)	50(100)	70(140)	~0
Sodium Hypochlorite	20(40)	20(40)	20(40)	~0	~0
Mercury	<0.05(<0.1)	$<1 \times 10^{-3}$ $(<2 \times 10^{-3})$	$<7 \times 10^{-5}$ $(<1.4 \times 10^{-4})$	$<7 \times 10^{-5}$ $(<1.4 \times 10^{-4})$	~0

Level A -- Reduction of mercury to less than 1×10^{-3} kg/kkg.

Level B -- Reduction of mercury to less than 7×10^{-5} kg/kkg.

Level C -- Level B + catalytic conversion of sodium hypo chlorite to sodium chloride. Plant 098 is at this level.

Level D -- Level C + evaporation and reuse of sodium chloride. No effluent except cooling water from system. Drying sulfuric acid to other use or concentration.

TABLE 50.

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: Diaphragm Cell, Chlor-Alkali (1810 kkg/day (2000 ton/day) Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	45,000	65,000	495,000*	1,500,000
Annual Costs:				
Interest + Taxes and Insurance	2,250	3,250	3,250	75,000
Depreciation	4,500	6,500	6,500	150,000
Operating and Maintenance Costs (excluding energy and power costs)	24,000	224,000	224,000	224,000
Energy and Power Costs		1,000	1,000	1,000
Total Annual Cost	30,750	234,750	234,750	450,000

Effluent Quality:

Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Calcium Carbonate sludge	12.25(24.5)	0	0	0	0
Sodium Hypochlorite	7.5(15)	7.5(15)	7.5(15)	0	0
Spent Sulfuric Acid	4(8)	4(8)	0	0	0
Chlorinated Hydrocarbons	0.7(1.4)	0.7(1.4)	0	0	0
Sodium Chloride	25.5(51)	25.5(51)	5(10)	5(10)	0
Sodium Hydroxide	22(44)	22(44)	4.5(9)	4.5(9)	0

Level A -- Settling Pond.

Level B -- Chlorinated hydrocarbons to disposal pit + sulfuric acid to sales, neutralization of sodium hydroxide and brine returned to system.

Level C -- Installation of chlorine burning hydrochloric acid plant for chlorine tail gas. Hydrochloric acid value equal to cost.

Level D -- Non-contact cooling substituted for barometric condensers - rough estimate.

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*Cost of installation -- 0 contribution to cost -- see Level C note.

attaining no discharge of process waste water pollutants are proximately $0.55/kkg ($0.50/ton) of product. For new facilities the cost would be considerably less, since non-contact condensers should be used in place of barometric condensers.

Additional energy requirements are negligible.

Hydrochloric Acid

During normal operation the chlorine-burning hydrochloric acid manufacturing process has no water-borne wastes. Startup wastes are less than 0.5 kg/kkg (1.0 lb/ton) of product and are typically neutralized in sodium hydroxide solutions. Cost effectiveness information is given in Table 51 using plant 121 as a model. Addition of a small sodium hypochlorite destruction vessel plus a pump and transfer line for reuse in the chlor-alkali eliminates the process waste water discharge from the process. Total cost for zero effluent attainment is $0.33/kkg ($0.30/ton) of product, while the incremental cost for going from typical to zero effluent treatment levels is $0.055/kkg ($0.05/ton). Additional energy requirements are negligible.

Hydrofluoric Acid

Hydrofluoric acid production, like that of the other mineral acids, generates a very low water-borne waste load. Good engineering, maintenance and housekeeping reduces the waste effluent to 0.5 kg/kkg (1.0 lb/ton) or less. A complete recycle zero discharge plant (152) of 27 kkg/day (30 ton/day) capacity and 15 years age, is chosen for cost effectiveness calculations as given in Table 48, column 4 (alternate B).

The large cost differential between Level C and Level B shows that two different approaches make a substantial difference in the costs involved. Plant 011 follows stoichiometric use of sulfuric acid, thereby eliminating $30,000 neutralization chemical costs per year. It handles calcium sulfate and calcium fluoride dry by hauling to a land dump, thereby eliminating pond settling and dredging costs for another $70,000/yr differential. In-process changes account, therefore, for a $7.70/kkg ($7/ton) difference in treatment costs.

Total cost to achieve no discharge of process waste water pollutants from plant 011 is $17.60/kkg ($16/ton) and for plant 152 is $14.30/kkg ($13/ton). The greatest portion of this cost is for handling and disposal of solid calcium sulfate, which has to be done in all plants.

Additional energy required for going from base level treatment to closed cycle operation is negligible. An additional 7.5 kw-hr (10 hp-hr) is allowed for pumping from collection ponds back to the system. This gives 5.3×10^7 kg cal (2.10×10^8 BTU) or

TABLE 51:

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: Hydrochloric Acid (36 kkg/day (40 tons/day) Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:		A	B*	C	D
Investment		10,000	10,000	15,000	15,000
Annual Costs:					
Interest + Taxes and Insurance		500	500	750	750
Depreciation		1,000	1,000	1,500	1,500
Operating and Maintenance Costs (excluding energy and power costs)		2,000	2,000	2,000	2,000
Energy and Power Costs		~0	~0	~0	~0
Total Annual Cost		3,500	3,500	4,250	4,250
Effluent Quality:					
Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Chlorine & Hydrogen Chloride	0.5(1)	0.75(1.5)	0.75(1.5)*	0	0

Levels A and B -- Neutralization in sodium hydroxide solution followed by discharge to surface water.

Levels C and D -- Destruction of sodium hypochlorite in small pond or vessel and use of sodium chloride solution in chlor-alkali system. Chlorine-burning hypochloric acid units are always located in chlor-alkali complexes.

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*This corresponds to exemplary plant operation with wastes only during startup. Level I guideline recommendation modelled to C.

TABLE 52.

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: **Hydrofluoric Acid (36 kkg/day (40 tons/day) Capacity)**

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B*	C	Alternate B**
Investment	0	30,000	50,000	75,000
Annual Costs:				
Interest + Taxes and Insurance	0	1,500	2,500	3,750
Depreciation	0	3,000	5,000	7,500
Operating and Maintenance Costs (excluding energy and power costs)	50,000	52,000	60,000	165,000
Energy and Power Costs	~0	~0	1,000	5,000
Total Annual Cost	50,000	56,500	68,500	181,250

Effluent Quality:

Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Calcium Sulfate	3650(7300)	0	0	0	0
Sulfuric Acid	110(220)	0	0	0	0
Calcium Fluoride	62.5(125)	0.5(1)	0.25(0.5)	0	0
Hydrogen Fluoride	2.5(5)	2.5(5)	0.25(0.5)	0	0
Hydrofluorosilicic Acid	12.5(25)	12.5(25)	0	0	0
Silicon Dioxide	12.5(25)	12.5(25)	0	0	0

Level A -- Land dumping of calcium sulfate, minimizing acid by operating near stoichiometry requirements. Costs are all for trucking of calcium sulfate, calcium fluoride and contained sulfuric acid to land dump.

Level B -- Similar to Exemplary Plant 011 of this study.

Level C -- Closed loop extension of 011.

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*Exemplary plant operation, Level I guideline recommendation based on modelling to Level C, or equivalent to alternate Level B.

**Exemplary closed loop plant 152 (27 kkg/day).

795/1/yr (210 gal/yr) of fuel oil. Total industry additional energy requirements are 8.30 x 10^8 kg cal (3.3 x 10^9 BTU).

Hydrogen Peroxide

a) Organic process

The waste water effluent resulting from the manufacture of hydrogen peroxide by the organic process contains waste hydrogen peroxide plus an organic solvent. The nature of this solvent is regarded as a trade secret.

Cost effectiveness information is developed in Table 53 for exemplary plant 069, a twenty year old, 85 kkg/day (94 ton/day) facility.

Estimated additional cost to attain zero waste discharge is approximately $1.10/kkg ($1.00/ton) of hydrogen peroxide.

Additional energy requirements are negligible.

b) Electrolytic process

Hydrogen peroxide may be produced using an electrolytic process. Twenty year old plant 100 serves as the basis for the cost effectiveness information shown in Table 54.

Elimination of the process waste water discharge from this plant would cost approximately $0.28 to $0.83/kkg ($0.25 to $0.75/ton) of product produced.

Additional energy required would be 2.2 x 10^8 kg cal (8.7 x 10^8 BTU).

Nitric Acid

There is no water-borne waste from the nitric acid manufacturing process, nor is there usually any contribution from air pollution treatment equipment. Only leaks, spills, monitoring and containment costs are involved.

For seven year old, 281 kkg/day (310 ton/day) plant 114, there are no effluent waste streams except boiler and cooling tower blowdowns. These are over 378,500 l/day (100,000 gal/day) in volume. Ancillary streams, however, are excluded from process waste water guidelines. Since no cost figures are available for nitric acid, they are estimated to be the same as those for sulfuric acid isolation and containment, $160,000. Applying this cost to the 288 kkg/day (320 ton/day) plant gives $0.24/kkg ($0.22/ton) cost for isolation and containment of leaks and spills. No energy addition is involved.

TABLE 53'.

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: **Hydrogen Peroxide (Organic Process) (85 kkg/day (94 tons/day) Capacity)**

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B*	C	D
Investment	23,000	53,000	200,000	0
Annual Costs:				
Interest + Taxes and Insurance	1,150	2,650	10,000	10,000
Depreciation	2,300	5,300	20,000	20,000
Operating and Maintenance Costs (excluding energy and power costs)	3,000	3,000	5,000	5,000
Energy and Power Costs	~0	~0	~0	~0
Total Annual Cost	6,450	10,950	35,000	35,000

Effluent Quality:

Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Organics	0.25(0.5)	0.1(0.2)	0.025(0.05)	0	0
Hydrogen Peroxide	20(40)	5(10)	5(10)	0	0

Level A -- Reduction of hydrogen peroxide with scrap iron, organics removal by mechanical separation.

Level B -- Level A + improved organics removal and spill containment.

Level C -- Closed loop process water, non-contact cooling water only effluent.

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*Not exemplary plant, modeled.

TABLE 54.

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: **Hydrogen Peroxide - Electrolytic (12 kkg/day (13.2 ton/day) Capacity)**

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	-	12,500	15,000	
Annual Costs:				
Interest + Taxes and Insurance	-	625	750	
Depreciation	-	1,250	1,500	
Operating and Maintenance Costs (excluding energy and power costs)	-	1,600	2,000	
Energy and Power Costs	-	~0	1,000	
Total Annual Cost	-	3,475	5,250	

Effluent Quality:

Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels		
Sodium Sulfate	0.75(1.5)	0.75(1.5)	0.75(1.5)	~0
Ammonium Sulfate	0.75(1.5)	0.75(1.5)	0.75(1.5)	~0

Level A -- There is no typical plant.
Level B -- Present plant operation
Level C -- Distillation to dryness 1136 liters/day (300 GPD)

Potassium Metal

There are no process, air pollution or ancillary water wastes involved in the production of potassium metal.

Potassium Chromates

Potassium dichromate is made from the reaction of sodium dichromate with potassium chloride. There is none of the massive ore waste present as in the sodium dichromate process. The only water-borne wastes from the exemplary 25 year old, 13.5 kkg/day (15 ton/day) plant 002 are from once-through cooling water used on the barometric condensers. Replacement of these condensers with non-contact heat exchangers, as planned for 1974, will eliminate the discharge of process waste water pollutants from this plant. Cost for this conversion is estimated at $60,000. See Table 55.

The treatment differential in going from base Level A to zero discharge costs $5.12/kkg ($4.65/ton) of potassium dichromate.

Energy requirements for pumps, filters, centrifuges, and other equipment are taken as 7.5 kw-hr (10 hp-hr) or 5.3×10^{7} kg cal/yr (2.1×10^{8} BTU/yr). Entire industry additional energy is estimated at the same value.

Potassium Sulfate

The treatment and control cost effectiveness values for potassium sulfate based on plant 118 are developed in Table 56.

Costs for going from base treatment to zero effluent is $2.38/kkg ($2.16/ton) of potassium sulfate.

There is a relatively high energy recovery process with 6.7×10^{10} kg cal (2.65×10^{11} BTU) or 1,000,000 l (265,000 gal) of fuel oil energy per year. For the entire industry the additional energy requirement is 1.72×10^{11} kg cal (6.8×10^{11} BTU).

Sodium Bicarbonate

Water-borne wastes from sodium bicarbonate facilities are small. Using plant 166 as a model, cost effectiveness values are developed in Table 57. Reducing the bicarbonate wastes to zero should be virtually cost free since current product losses should cover expenses.

There are no significant new energy requirements.

TABLE 55.

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: Potassium Chromate (13.5 kkg/day (15 tons/day) capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B*	C	D
Investment	20,000	50,000	110,000	110,000
Annual Costs:				
Interest + Taxes and Insurance	1,000	2,500	5,500	5,500
Depreciation	2,000	5,000	11,000	11,000
Operating and Maintenance Costs (excluding energy and power costs)	0	10,000	10,000	10,000
Energy and Power Costs	0	1,000	1,000	1,000
Total Annual Cost	3,000	18,500	27,500	27.500

Effluent Quality:

Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Sodium Chloride	400(800)	400(800)	0	0	0
Filter Aid	0.85(1.7)	~0.05(~0.1)	0	0	0
Potassium Dichromate	~0.5(~1)	~0.5(~1)	~0.5(~1)	~0	~0

Level A -- Discharge of all water to settling pond to remove filter aid.

Level B -- Centrifuge, filter, pumps, piping and installation for sodium chloride and filter aid removal. Salt value has been assumed zero.

Level C -- Non-contact heat exchangers installed.

---

*Exemplary plant, Level I guidelines recommendations modelled to Level C, plans for 1974 for exemplary plant.

TABLE 56.

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: **Potassium Sulfate (454 kkg (500 tons) per day Capacity)**

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	40,000	700,000	700,000	700,000
Annual Costs:				
Interest + Taxes and Insurance	2,000	35,000	35,000	35,000
Depreciation	4,000	70,000	70,000	70,000
Operating and Maintenance Costs (excluding energy and power costs)	10,000	124,000	124,000	124,000
Energy and Power Costs	~0	166,000	166,000	166,000
Total Annual Cost	16,000	395,000	395,000	395,000

Effluent Quality:

Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Ore Muds	15(30)	0	0	0	0
Waste Liquor	2000(4000)	2000(4000)	0	0	0

Level A -- Pond settling of muds. Discharge of dissolved solids to surface water.

Level B -- Evaporation to recover liquor chemicals and water + Level A value of recovered chemicals not deducted from costs. Water value is also not deducted.

TABLE 57.

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: **Sodium Bicarbonate (272 kkg/day (300 ton/day) Capacity)**

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	10,000	15,000	15,000	15,000
Annual Costs:				
Interest + Taxes and Insurance	500	750	750	750
Depreciation	1,000	1,500	1,500	1,500
Operating and Maintenance Costs (excluding energy and power costs)	1,000	2,000	2,000	2,000
Energy and Power Costs	~0	~0	~0	~0
Total Annual Cost	2,500	4,250	4,250	4,250

Effluent Quality:

Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Sodium Carbonate	30(76)	38(76)	38(76)	0	0
Sodium Bicarbonate	10(20)	10(20)	0	0	0
Rubbish	<2.5(<5)	0	0	0	0

Level A -- Settling pond, landfill for rubbish, discharge to surface water.

Level B -- Redissolve broken bags and waste sodium bicarbonate + Level A.

Level C -- Recycle sodium carbonate to Solvay Process system. Value obtained equal cost.

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*Exemplary plant plans to go to Level C in near future, hence Level I guidelines recommendations were modelled to Level C.

Sodium Carbonate

The Solvay process produces approximately 1370 kg (3000 lb) of dissolved solid wastes for every kkg (ton) of product. These solids consist of slightly over 0.91 kkg (1.0 ton) of calcium chloride, which has high solubility, is difficult to obtain in anhydrous form, and spontaneously picks up moisture from the air when land dumped, and about 0.45 kkg (0.5 ton) of unreacted sodium chloride, also highly soluble.

Although there is a market for calcium chloride, this market can be supplied with 10 to 15 percent of the calcium chloride available from Solvay plants alone. Therefore, most of the available calcium chloride must be disposed of at zero value or less (disposal costs). The sodium chloride can be reused if it can be separated from the calcium chloride and other wastes, but the value of this raw material is low and recovery is uneconomical. Therefore, half a dozen Solvay plants discharge more waste to surface water than any other chemical subcategory and there is no general economically feasible treatment scheme to eliminate the discharge of these wastes. Costs are given below for Solvay process plant 166. This 2520 kkg/day (2800 ton/day), over 75 year old facility, is used for cost developments.

Treatment and Control Method	Capital Costs $	Annual Cost $
1. Coproduction of ammonium chloride with soda ash	34,000,000	26,000,000
2. Ammonia and hydrogen chloride from ammonium chloride	133,000,000	45,000,000
3. Ammonia and chlorine from ammonium chloride	80,000,000	34,000,000
4. Deep well disposal	6,000,000	1,600,000
5. Total evaporation plus ocean barging of solid wastes	51,000,000	31,000,000

Options 1, 2, and 3 are process changes or additions with high capital investments. The quantities of ammonium chloride, hydrogen chloride and chlorine produced either exceed the current demand or would be such major contributors that the market structure would be drastically altered. The other two options are disposal methods.

The only economically feasible disposal options for Solvay process soda ash wastes today are partial recovery of calcium chloride for sales or deep welling. Since the Solvay soda ash wastes are similar to those for brine salts and oil well salts, which are extensively deep-welled, a good case can be made for such disposal, if geologically feasible at the plant location (or close by). However, deep-well disposal may be practiced only under strictly regulated conditions, consistent with State and Federal laws.

Cost effectiveness values are developed using these two technologies in Table 58.

Additional costs for zero discharge of wastes to surface water are approximately \$0.55/kkg (\$0.50/ton) of product. For deep-welling disposal alone, costs for zero waste effluent are \$1.76/kkg (\$1.60/ton) produced. Additional energy requirements, primarily for calcium chloride recovery, are high. Estimated requirements for plant 166 are 3.15 x 10^{11} kg cal/yr (1.25 x 10^{12} BTU/yr) or for the entire industry 1.26 x 10^{12} kg cal/yr (5.0 x 10^{12} BTU/yr). Without calcium chloride recovery, about 1.25 x 10^{10} kg cal/yr (5.0 x 10^{12} BTU/yr) for plant 166 or 5.0 x 10^{10} kg cal/yr (2.0 x 10^{11} BTU/yr) for the industry, would be needed for deep welling.

Sodium Chloride

a) Solar evaporation process

It has been recommended that concentrated magnesium-rich residual brines or bitterns from solar salt manufacture be stored and eventually recovered for their chemical value. Taking Plant 059 as a model, cost effectiveness values are developed in Table 59.

One 146 ha (360 ac) pond is needed each year. While this storage capacity is available for the next five to ten years, obviously it cannot go on indefinitely. Use of these valuable mineral deposits should be made in the near future. Storage costs for solar salt bitterns for Plant 059 are \$2.42/kkg (\$2.20/ton) of product.

Additional energy requirements are negligible.

b) Solution brine-mining process

Unlike the solar salt industry where all wastes are stored or disposed of in surface ponds, salt producers using the brine-mining process get their salt from underground deposits and return most wastes to the mine deposit.

Exemplary plant 030, a 49 year old, 1,000 kkg/day (1,100 ton/day) facility is used for cost effectiveness developments in Table 60. Complete elimination of process wastes in the plant effluent would cost, for a new plant, approximately \$0.28/kkg (\$0.25/ton) of product. This assumes plant 030 technology plus initial installation of non-contact final condensers. Conveying and packing losses may recovered dry and either reused or land (or well) disposed.

Elimination of all but 1 kg/kkg (2 lb/ton) waste from plant 030 would cost approximately \$0.55/kkg (\$0.50/ton) of product.

TABLE 58.

Water Effluent Treatment Costs
Inorganic Chemicals
Chemical: **Soda Ash (2520 kkg/day (2800 tons/day) Capacity)**

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	500,000	21,500,000	27,500,000	27,500,000
Annual Costs:				
Interest + Taxes and Insurance	25,000	1,075,000	1,375,000	1,375,000
Depreciation	50,000	2,150,000	2,750,000	2,750,000
Operating and Maintenance Costs (excluding energy and power costs)	375,000	3,175,000	3,675,000	3,675,000
Energy and Power Costs	-	800,000	1,000,000	1,000,000
Total Annual Cost	450,000	(1,080,000) Profit	520,000	520,000

Effluent Quality:

Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Calcium Chloride	1100(2200)	1100(2200)	900(1800)	0*	0*
Sodium Chloride	500(1000)	500(1000)	500(1000)	0*	0*
Calcium Carbonate	85(170)	~0	~0	0*	0*
Calcium Oxide	135(270)	25(50)	25(50)	0*	0*
Calcium Sulfate	31(62)	2.5(5)	2.5(5)	0*	0*
Ash and cinders	40(80)	~0	~0	0*	0*
Silicon Dioxide	585(117)	~0	~0	0*	0*

Level A -- Settling ponds
Level B -- Level A + evaporation of 20% of stream to recover calcium chloride for sale at $44/kkg ($40/ton) -- 8,280,000 value.
Level C -- Level B + deep well disposal.

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*No surface water effluent.

TABLE 59 .

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: **Solar Salt (2540 kkg/day (2800tons/day) Capacity)**

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	14,400,000	14,400,000	14,400,000	14,400,000
Annual Costs:				
Interest + Taxes and Insurance	720,000	720,000	720,000	720,000
Depreciation	1,440,000	1,440,000	1,440,000	1,440,000
Operating and Maintenance Costs (excluding energy and power costs)	~0	~0	~0	~0
Energy and Power Costs	~0	~0	~0	~0
Total Annual Cost	2,160,000	2,160,000	2,160,000	2,160,000

Effluent Quality:

Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Bitterns	70,000(140,000)	0	0	0	0

Level A -- 1 new 360 acre unlined pond per year is needed. Costs are taken from Section VIII for unlined ponds.

TABLE 60.

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: **Sodium Chloride (Brine/Mining) (1000 kkg/day (1100 ton/day) Capacity**

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	-	500,000	1,000,000	600,000
Annual Costs:				
Interest + Taxes and Insurance	-	25,000	50,000	30,000
Depreciation	-	50,000	100,000	60,000
Operating and Maintenance Costs (excluding energy and power costs)	-	10,000	10,000	10,000
Energy and Power Costs	-	~0	~0	~0
Total Annual Cost	-	85,000	160,000	100,000

Effluent Quality:

Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Sodium Chlorine	50(100)	-	6(12)	1(2)	~0
Brine Sludge	2.5(5)	-	0	0	~0

Level A -- No information.

Level B -- Plant 030 technology, sludge returned to wells. Control system developed including $425,000 damming, curbing, collection and pumping to wells, and $63,000 instrumentation and miscellaneous pumps and piping.

Level C -- Level B + non-contact heat exchangers for barometric condensers.

Level D -- For new plants. Elimination of conveying and packing station losses peculiar to Plant 030.

Negligible additional energy would be required.

Sodium Dichromate

The sodium dichromate manufacturing process produces a waste stream containing high concentrations of suspended and dissolved solids primarily because of the chromium treatment process used. Two year old 149 kkg/day (164 ton/day) plant 184 is used as the model for cost effectiveness development as shown in Table 61.

Additional cost above typical treatment is \$17.60/kkg (\$16/ton) of product, of which \$13.20/ (\$12/ton) is already being spent in exemplary plant 184. Evaporation to recover dissolved salts costs \$4.40/kkg (\$4/ton) of product. Selling price of sodium dichromate is \$380/kkg (\$345/ton).

These figures illustrate the high cost of isolating, containing, treating and disposing harmful wastes. They also show that if the effluent streams can be kept small, 1,317 cu m/day (348,000 gal/day) in this case, removal of dissolved salts by evaporation is expensive, but not prohibitively so.

It is believed that, while the isolation, containment and treatment facilities of exemplary plant 184 are exceptional, there are more economical ways of achieving the same degree of chromium reduction.

Additional energy requirements are estimated to be 2.5 x 10^{10} kg cal (1.0 x 10^{11} BTU) per year for plant 184. For the industry, using similar treatment (which is doubtful) to to eliminate the discharge of process waste water pollutants, the additional yearly energy requirements would be 6.05 x 10^{10} kg cal (2.4 x 10^{11} BTU).

Sodium Sulfate

Sodium sulfate is a by-product of sodium dichromate and other manufacturing processes. As such, no water-borne wastes are attributed to its production. Therefore, it is considered to be a zero effluent-zero treatment and control chemical with no additional energy requirements.

Sodium Metal

Sodium metal and chlorine are produced as coproducts in the Downs Cell process. Since the chlorine produced is handled similarly and has the same wastes as the mercury and diaphragm cell processes, only wastes specific to the Downs Cell and sodium production are included here. Table 62 gives the estimated cost effectiveness values for a 58 kkg/day (65 ton/day) fourteen year old plant (096).

TABLE 61 .

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: **Sodium Dichromate (149 kkg/day (164 tons/day) Capacity)**

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	100,000	1,000,000	1,800,000	1,800,000
Annual Costs:				
Interest + Taxes and Insurance	5,000	5,000	90,000	90,000
Depreciation	10,000	100,000	180,000	180,000
Operating and Maintenance Costs (excluding energy and power costs)	~0	560,000	610,000	610,000
Energy and Power Costs	~0	4,000	64,000	64,000
Total Annual Cost	15,000	669,000	944,000	944,000

Effluent Quality:

Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Total Suspended Solids	900(1800)	0.125(0.25)	0.125(0.25)	~0	~0
Total Dissolved Solids	88.5(177)	88.5(177)	88.5(177)	~0	~0
Chromium 6	-	-	0.0001(0.0002)	~0	~0

Level A -- Settling pond.

Level B -- Segregation and chemical treatment for chromium-6. Pond settling and discharge of clear effluent to surface water.

Level C -- Level B + evaporation to recover dissolved sodium chloride. Recovered sodium chloride costed as zero value. Closed loop operation.

TABLE 62.

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: **Sodium Metal (58 kkg/day (65 tons/day) Capacity)**

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	0	400,000	700,000	0
Annual Costs:				
Interest + Taxes and Insurance	0	20,000	35,000	35,000
Depreciation	0	40,000	70,000	70,000
Operating and Maintenance Costs (excluding energy and power costs)	4,000	4,000	10,000	10,000
Energy and Power Costs	~0	~0	~0	~0
Total Annual Cost	4,000	64,000	115,000	115,000

Effluent Quality:

Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Sodium Chloride	57.5(115)	57.5(115)	57.5(115)	~0	~0
Misc. Alkaline Salts	30(60)	30(60)	30(60)	~0	~0
Bricks, Anodes, Other Solids	≤2.5(≤5)	0	0	0	~0

Level A -- Disposal of salts plus solids.
Level B -- Facilities for separating salts from solids.
Level C -- Containment, isolation and return of salts to brine system.

Costs for plant 096 to attain a zero water-borne waste effluent are \$2.47/kkg (\$2.25/ton) of sodium above initial expenditures of \$3.30 to \$4.40/kkg (\$3 to \$4/ton) of sodium, which is currently selling for \$412/ kkg (\$375/ton).

Additional energy costs should be negligible.

Sodium Silicate

The wastes from the sodium silicate manufacturing process are relatively small and closed loop operation has been achieved in plant 072.

For the purpose of developing cost effectiveness data plant 134 has been selected for Table 63 calculations. This plant is a ten year old, 72 kkg/day (80 ton/day) facility. Control and treatment costs are approximately \$1.00/kkg (\$0.90/ton) of product.

Additional energy costs using this approach are 3.5×10^9 kg cal (14×10^{10} BTU). For the total industry, additional energy requirements are 8.4×10^{10} kg cal (3.32×10^{11} BTU).

A second approach using only Level A treatment and closing the loop bypasses both the energy requirements and most of the cost. This approach is used in plant 072. Treatment costs for this approach would be approximately \$0.22/kkg (\$0.20/ton) of product.

Costs for both approaches are reasonable. In view of the energy advantage for plant 072's approach, this recycle method should be favored.

Sodium Sulfite

The wastes from the sodium sulfite processes are essentially sodium sulfite. Table 64 gives the cost effectiveness values for plant 168, a fifteen year old installation.

Costs for reducing the waste water discharge from plant 168 to zero are approximately \$2.75/kkg (\$2.50/ton) of product. If recovery of sodium sulfite is directed at the same stream which is now treated and directly discharged, there is a potential for \$25,000/yr profit. Plants not now treating or recovering sodium sulfite should explore this approach.

Additional energy required is approximately 1.62×10^9 kg cal/yr (6.4×10^9 BTU/yr) or 24,200 l (6400 gal) of fuel oil /yr. For the entire industry this would be 2.92×10^{10} kg cal (1.16×10^{10} BTU).

TABLE 63.

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: **Sodium Silicate (72 kkg/day (80 tons/day) Capacity)**

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B*	C*	D
Investment	26,000	42,000	62,000	62,000
Annual Costs:				
Interest + Taxes and Insurance	1,300	2,106	3,100	3,100
Depreciation	2,600	4,200	6,200	6,200
Operating and Maintenance Costs (excluding energy and power costs)	1,000	9,000	10,000	10,000
Energy and Power Costs	~0	--	10,000	10,000
Total Annual Cost	4,900	15,300	29,300	29,300

Effluent Quality:

Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Sodium Silicate	2(4)	2(4)	2(4)	0	0
Sodium Sulfate	2.5(5)	2.5(5)	2.5(5)	0	0
Filter Aids	2(4)	0	0	0	0
Sand	0.5(1)	0	0	0	0
Sodium Hydroxide	0.5(1)	0.5(1)	0	0	0

Level A -- Settling pond only.
Level B -- Settling pond plus neutralization (existing good plant).
Level C -- Evaporation to remove and recover dissolved solids + Levels A and B treatment. Sodium silicate recovered (exemplary plant).

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*Note Level C is exemplary plant level in this table.

TABLE 64.

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: **Sodium Sulfite (45 kkg/day (50 ton/day) Capacity)**

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	0	250,000	275,000	150,000
Annual Costs:				
Interest + Taxes and Insurance	0	12,500	13,750	7,500
Depreciation	0	25,000	27,500	15,000
Operating and Maintenance Costs (excluding energy and power costs)	0	10,000	12,000	5,000
Energy and Power Costs	0	2,000	7,000	6,000
Total Annual Cost	0	49,500	47,750	(25,000) Profit

Effluent Quality:

Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Sodium Sulfate	-	-	29(58)	0	0
Sodium Sulfite	30.5(61)	30.5(61)	1.5(3)	0	0

Level A -- No treatment -- typical for industry.
Level B -- Full treatment system, but dissolved solids still discharged.
Level C -- Level B + evaporation recovery and sales of recovered product. Product value $12,500.
Level D -- Isolation and containment parts of complete system of Level B + evaporation to recover sodium sulfite. Product value is $58,500.

Sulfuric Acid

The sulfuric acid (sulfur-burning) manufacturing process has no process wastes. The only water-borne wastes result from leaks, spills, air pollution control equipment, and ancillary operations such as cooling tower blowdowns and ion-exchange regenerants. Since cooling tower blowdowns and ion-exchange regenerants are not considered to be process waste water, they are not included here. Air pollution control equipment costs are presented for informational purposes.

Regen plants for making sulfuric acid from waste or spent acid are not covered in this study but are included in cost effectiveness development for informational purposes.

Exemplary sulfur-burning plant 141, a three year old, 360 kkg/day (400 ton/day) plant, was used as the model in Table 65.

Costs are less than $0.10/kkg ($0.10/ton) of product. Additional energy is negligible.

Titanium Dioxide

a) Chloride process

Most chloride processes for titanium dioxide production use either rutile or "synthetic rutile" ore. One plant uses lower-grade ores but for the purposes of this cost effectiveness discussion, this process is considered to be on-site beneficiation plus a "synthetic rutile" process.

Currently, chloride process wastes are treated or disposed of by complete neutralization, deep-welling and ocean barging. For companies already ocean barging, cost run $5.50 - $11 kkg ($5 to $10 per ton) of titanium dioxide product. For those starting barging a location further from the ocean, or requiring extensive shore facilities, the costs may range from $11 to $22/kkg ($10 to $20/ton).

Deep-welling costs run from $2.20 to $5.50/kkg ($2 to $5/ton) of titanium dioxide product. Complete neutralization, on the other hand, is much more expensive. Table 66 shows the cost effectiveness development for this approach using ten year old 67 kkg/day (74 ton/day) exemplary plant 009 as the model.

Complete neutralization which is now done by plant 009 costs $40/kkg ($36/ton) differential over base treatment Level A.

Reduction to virtually zero discharge of wastes costs $71/ kkg ($64/ton) of product. Titanium dioxide sells for $605 to $627/kkg ($550 to $570/ton).

Additional energy costs are roughly estimated to be 1.3 x 10^{10} x 10^{10} kg cal (5.0 x 10^{10} BTU) for plant 009 and 1.7 x 10^{11} kg cal

TABLE 65.

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: **Sulfuric Acid (Sulfur Burning)(360 kkg/day (400 tons/day) Capacity)**

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	50,000	100,000	160,000	160,000
Annual Costs:	2,500	5,000	8,000	8,000
Interest + Taxes and Insurance	5,000	10,000	16,000	16,000
Depreciation	~0	~0	~0	~0
Operating and Maintenance Costs (excluding energy and power costs)	~0	~0	~0	~0
Energy and Power Costs	7,500	15,000	24,000	24,000
Total Annual Cost				

Effluent Quality:

Effluent Constituents Parameters (Units) kg/kkg(Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Spills, Leaks	1(2)	0.5(1)	0	0	0

Closed Cycle System

Level A -- Typical diking and containment.

Level B -- Good isolation and containment + Level A.

Level C -- Lined containment emergency pond -- 0.4 hectare (1 acre) + Level A and B.

TABLE 66.

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: **Titanium Dioxide (Chloride Process), 67 kkg (74 ton) per day basis**

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	300,000	4,000,000	5,300,000	5,300,000
Annual Costs:				
Interest + Taxes and Insurance	15,000	200,000	265,000	265,000
Depreciation	30,000	400,000	530,000	530,000
Operating and Maintenance Costs (excluding energy and power costs)	10,000	390,000	890,000	890,000
Energy and Power Costs	~0	10,000	45,000	45,000
Total Annual Cost	55,000	1,000,000	1,730,000	1,730,000

Effluent Quality:

Effluent Constituents Parameters (Units) **kg/kkg (Pounds/Ton)**	Raw Waste Load	Resulting Effluent Levels			
Iron Hydroxides	65(130)	65(130)	~0	~0	~0
Other metal oxides	65(130)	65(130)	~0	~0	~0
Ore	138(276)	~0	~0	~0	~0
Titanium hydroxides	25(50)	29(58)	~0	~0	~0
Hydrochloric Acid	227(454)	227(454)	~0	~0	~0
Titanium Dioxide	40.5(81)	~0	~0	~0	~0
Coke	23(46)	~0	~0	~0	~0
Soluble Chlorides and sulfates	-	-	315(630)	~0	~0

Leval A -- Pond settling.
Level B -- Complete chemical treatment facility + land dumping of solid waste.
Level C -- Level B + specialty unit demineralization + evaporation of regenerant solution.
Level D -- Same as Level C.

(6.75×10^{11} BTU) for the entire industry using the same treatment.

b) Sulfate process

The sulfate process for producing titanium dioxide has the heaviest water-borne waste load per ton of product of all the processes of this study. Of the approximately three kkg waste/kkg of product, two kkg are sulfuric acid. The model plant used is plant 142, a twenty-seven year old 108 kkg/day (120 ton/day) facility. Cost effectiveness is developed in Table 67.

Additional costs in going from typical Level A to virtually complete elimination of water-borne wastes are $106/kkg ($96/ton) or 10.5¢/kg (4.8¢/lb) of titanium dioxide produced. Going to Level C costs $90/kkg ($82/ton) or 9.0¢/kg (4.1¢/lb).

This is compared to $8.80 to $11.0/kkg ($8 to $10/ ton) for ocean barging of strong acid wastes. Adding Level B costs of approximately $11/kkg ($10/ton) to this gives about $22/kkg ($20/ton) for removal of acidity and the largest portion of the wastes. Ocean barging, as mentioned for the chloride process, can range for new plants (or old plants not now using this disposal means) up to $33/kkg ($40/ton) or $44/kkg ($40/ton) overall waste costs. Thus, ocean barging costs about one-fourth to one-half that of complete neutralization.

Acid recovery is another attractive approach. Using a current EPA-support pilot plant as model for acid recovery, cost effectiveness is developed in Table 68. Additional costs for this approach are $53/kkg ($48/ton) of titanium dioxide produced for practically zero water-borne waste eliminating Level D. Without demineralization, additional costs above Level A are $37.50/kkg ($34/ton) or about onehalf that for complete neutralization.

Required additional energy for complete neutralization plus demineralization and evaporation of regenerant is 4.15×10^{10} kg cal/yr (4.0×10^{9} BTU/yr) for plant 142 and 1.35×10^{11} kg cal/yr (5.35×10^{11} BTU/yr) for the industry (sulfate process).

Similar values for acid recovery are 1.6×10^{11} kg cal (6.3×10^{11} BTU) for plant 142 and 1.32×10^{12} kg cal (5.2×10^{12} BTU) for the industry.

TABLE 67.

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: **Titanium Dioxide (Sulfate Process), 108 kkg (120 ton) per day basis**

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	100,000	150,000	11,200,000	11,500,000
Annual Costs:				
Interest + Taxes and Insurance	5,000	7,500	560,000	575,000
Depreciation	10,000	15,000	1,120,000	1,150,000
Operating and Maintenance Costs (excluding energy and power costs)	65,000	400,000	2,220,000	2,350,000
Energy and Power Costs	~0	~0	11,000	45,000
Total Annual Cost	80,000	422,500	4,011,000	4,120,000

Effluent Quality:

Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Sulfuric Acid	2025(4050)	2025(4050)	1745(3490)	~0	~0
Iron Sulfate	387(774)	387(774)	370(740)	~0	~0
Aluminum Sulfate	270(540)	270(540)	260(520)	~0	~0
Magnesium Sulfate	220(440)	220(440)	210(420)	~0	~0
Other metal suflates	35(70)	35(70)	35(70)	~0	~0
Solid Wastes	210(420)	20(40)	20(40)	~0	~0
Soluble Calcium Sulfate	-	-	-	265(530)	~0

Level A -- Settling Pond
Level B -- Level A + neutralization of weak acid stream.
Level C -- Full neutralization.
Level D -- Level C + specialty system demineralization + evaporation of regenerant solution.

TABLE 68.

Water Effluent Treatment Costs (Acid Recovery Option)

Inorganic Chemicals

Chemical: Titanium Dioxide (Sulfate Process), 108kkg (120/ton) per day basis

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	100,000	150,000	4,000,000	5,500,000
Annual Costs:				
Interest + Taxes and Insurance	5,000	7,500	200,000	275,000
Depreciation	1,000	15,000	400,000	550,000
Operating and Maintenance Costs (excluding energy and power costs)	65,000	400,000	500,000	850,000
Energy and Power Costs	~0	~0	400,000	445,000
Total Annual Cost	71,000	422,500	1,500,000	2,120,000

Effluent Quality:

Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Sulfuric Acid	2025(4050)	2025(4050)	1745(3490)	~0	
Iron Sulfate	387(774)	387(774)	370(740)	~0	~0
Aluminum Sulfate	270(540)	270(540)	260(520)	~0	~0
Magnesium Sulfate	220(440)	220(440)	210(420)	~0	~0
Titanium Sulfate	180(360)	180(360)	130(260)	~0	~0
Other metal sulfates	35(70)	35(70)	35(70)	~0	~0
Solid Wastes	210(420)	20(40)	20(40)	~0	~0
Soluble Calcium Sulfate	-	-	-	~200(~400)	~0

Level A -- Settling Ponds
Level B -- Level A + weak acid stream neutralization.
Level C -- Level B + acid recovery facilities.
Level D -- Level C + specialty system demineralization + evaporation of regenerant solution.

Summarizing the costs for rough comparison purposes gives:

Method	Cost/kkg (Cost/ton) Titanium Dioxide
Ocean barging and weak acid neutralization	$22 ($20)
Acid recovery	$44 ($40)
Total neutralization	$88 ($80)

Overlaps in costs can occur depending on specific circumstances. Since most of the neutralization products are insoluble calcium sulfate and metallic oxides and hydroxides, the complete neutralization of sulfate process wastes is a relatively "clean" process. Also, its simple tested technology reliability is attractive. Acid recovery is still in the development stage for the process described. Corrosion problems are the biggest current uncertainty. The cost of this approach is one-half that of complete neutralization, however, and there is no reason why technology know-how can not be brought to bear on this process.

GENERAL INFORMATION ON COST OF CONTROL AND TREATMENT SYSTEMS

Segregation of contaminated water streams from non-contaminated streams is the first step in water-borne waste abatement. Since the treatment costs normally depend on the volume of water to be treated more than the amount of waste, keeping the waste water volume small reduces costs and energy requirements. Spills, leaks and washdowns are small, but need to be contained and isolated.

Cost for segregation and containment vary depending on the size and complexity of the plant, volume and nature of the wastes, and the equipment employed.

Estimates of these costs based on information obtained from plant visits are given below. In general, small chemical plants produce 50 tons/day or less of product. However, this may vary significantly with the particular chemical.

Isolation of wastes containing mercury and chromium costs approximately $200,000 to $300,000. Large salt, acid and chlor-alkali plants also fall in a similar price range for isolation and containment costs. Older plants may be more difficult and expensive to modify than new facilities.

Isolation and Containment Costs

Purpose	Installations	Small Plants	Large Plants
Isolation	Trenches and sewers pipelines, sumps, catch basins, tanks and pumps	$ 10,000-100,000	$100,000-300,000
Containment	Dikes and curbing	$ 5,000-50,000	$ 50,000-200,000
Isolation	Non-contact heat-exchangers	$ 50,000	$100,000-500,000

Barometric condensers are the most common source of cooling water contamination. Barometric condensers are now being replaced by non-contract heat exchangers in various inorganic chemical plants.

Chemical Treatment Systems

Equipment Costs

These systems, consisting of chemical reactors, clarifiers, thickeners, and filters or centrifuges, are designed as integral units for complete waste treatment. Installed equipment costs for chemical treatment systems as a function of capacity are summarized below:

Capacity cu m/day (gal/day)	Reaction Tanks, $	Clarifiers and Thickeners, $	Filters or Centrifuges, $	Total* Costs $
38 (10,000)	15,000	15,000	25,000	60,000
379 (100,000)	25,000	40,000	25,000	150,000
3785 (1,000,000)	37,500	75,000	200,000	500,000
37850 (10,000,000)	50,000	200,000	750,000	2,000,000

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*Includes engineering, land preparation, and installation. Does not include land cost, storage tanks and disposal facilities, or other auxiliary equipment.

These costs are for light slurry loads. For heavy slurry loads, such as for titanium dioxide wastes, overall costs are several times greater.

Chemical Costs

The costs for chemical treatments cannot be generalized. Most of the chemicals used, however, are for neutralizations. Chemical treatments costs depend on the chemical used and the amount required, which varies with the particular situation. The unit cost of the chemical is usually known. Whenever feasible, neutralization of alkaline wastes is done with sulfuric acid. As shown in Table 69, sulfuric acid costs only 30 to 40 percent as much as hydrochloric and nitric acid. In other words, a dollars worth of sulfuric acid will neutralize 2.5 to 3.5 times as much alkalinity as a dollars worth of the other two acids. Cost for sulfuric acid is approximately $33/kkg ($30/ton).

Limestone and lime are commonly used to neutralize acidic waste streams. Limestone is the lower cost material at $7-11/kkg ($6-10/ton); but suffers the disadvantage of slower reaction, high impurities, and lower obtainable pH. Lime costs are approximately $22/kkg. Ammonia and sodium hydroxide are far more expensive than lime or limestone, with 50 percent sodium hydroxide at $121/kkg ($110/ton) (100 percent basis), it can be seen why lime is preferable in most cases.

For small usage or where solubility or character of precipitate is important, caustic soda or ammonia may still be employed.

Neutralizations with waste acids or bases can change the whole cost structure. Waste sulfuric acid is often available at either no cost or the cost of freight. Waste lime, caustic soda or ammonia can sometimes be obtained at similar low costs.

Costs for neutralizations and other chemical reactions are simply determined for special applications by multiplying the cost/weight of the neutralizing or reacting chemical by the weight stoichiometrically required. Where specific experience is available, it may have been found that 10 to 20 percent excess over stoichiometric quantities are needed. In rare cases, several-fold excesses may be used to ensure complete reaction.

Settling Ponds and Vessels

Ponds for storage, emergency discharge and containment, settling of suspended solids, or solar evaporation, are the most commonly employed treatment and control facility in the inorganic chemical industry. Two categories, unlined ponds and lined ponds, are summarized in the tables and figures of this section.

A third category, tanks and vessels such as thickeners and clarifiers, are not widely used at present in the inorganic chemical industry as contrasted to other chemical industries and sanitary treatment facilities. As land becomes more costly and unavailable and treatment and control requirements change, open tanks and vessels may see increased use. Cost information on equipment of this type has already been given in the chemical treatment section.

TABLE 69. Comparison of Chemicals for Waste Neutralization

Alkaline Wastes Neutralizing Material		Relative Chemical Cost*, $	kg*** Req'd/kkg Alkali**		
			$CaCO_3$	$Ca(OH)_2$	NaOH
Sulfuric Acid	(50° Be)	1.00	1260	1700	1580
Hydrochloric Acid	(20° Be)	2.57	2320	3140	2500
Nitric Acid	(39.5° Be)	3.51	2100	2840	2630

Acid Wastes Neutralizing Material	Cost*, $	kg*** Req'd/kkg Acid**		
		H_2SO_4	HCl	HNO_3
Lump limestone, high Ca	1.16	1100	1480	860
Lump limestone, dolomitic	1.00	940	1270	730
Pulv. limestone, high Ca	1.59	1100	1480	860
Oulv. limestone, dolomitic	1.37	940	1270	730
Hydrated lime, high Ca	3.06	790	1070	620
Hydrated lime, dolomitic	2.50	650	870	510
Pebble lime, high Ca	2.07	600	800	460
Pebble lime, dolomitic	1.87	540	730	420
Pulv. quicklime, high Ca	2.18	600	800	460
Pulv. quicklime, dolomitic	1.97	540	730	420
Sodium bicarbonate	20.65	1730	2330	1350
Soda ash	13.08	1190	1600	930
Caustic soda (50%)	9.96	1640	2200	1270
Ammonia (anhyd.)	5.90	350	470	270
Magnesium oxide	3.90	420	560	330

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*Delivered cost including freight.

**Commodity weight.

***To convert numbers to lbs. req'd/100 lbs alkali or acid, multiply x 0.1.

Unlined Ponds

The costs of constructing unlined ponds differ widely depending on the circumstances. Since they cover large areas, the cost of the land itself is a factor. Building a 200 hectare (500 ac) pond on prime industrial land may cost $1 to 5 million just for the land itself. No provision is made in this analysis, however, for such costs. It is assumed that the land value is not a large portion of the cost. For small ponds of less than 4 to 20 ha (10 to 50 ac) and land values of $250 to $625/ha ($100 to $250/ac), this assumption is good, as will be seen from the magnitude of the other costs.

Construction costs vary widely depending on the circumstances. Use is often made of natural pits, valleys, ponds, lakes, etc., for minor alterations, such as damming, dike building and leveling. Excavation is easier in some localities than others.

Pond size is also a major cost factor. Small ponds may be dug and the excavated dirt used for dikes. Large ponds are usually diked or dammed.

Assuming equal depths of two ponds, one large and one small, the volume increases as the square while the dike length (and earth moving) is increasing only linearly. Therefore, costs will be developed for small ponds and then for large ones.

Small pond capital costs are given in Figure 64.

Large pond costs developed from reference (27) are shown in Figure 65. Undoubtedly, many of these installations made use of natural topography (lakes, basins, etc.) to avoid as much excavation as possible. Nevertheless, the general cost levels and trends may be seen. As would be expected from the diking costs varying by the square root of the area, the pond costs per hectare above 200 ha (500 ac) change very slowly.

Lined Ponds

To avoid excessive liquid seepage, ponds are often lined with clay, concrete or other substances. Recently, however, new lining materials have come into use -- rubber and plastic sheeting.

Essentially, costs for pond construction are the same as for unlined ponds except for the sheeting material and installation. Therefore, the costs may be estimated by adding the installed liner costs to the previously determined costs for unlined ponds. The material costs for the lining range from $1.00 to $6.00/sq m (10¢ to 60¢/sq ft), depending on the material selected and the thickness of the sheet.(30) Although thicknesses as low as 250 microns (10 mils) have been discussed,(31) the most used thickness appears to be 750 micron (30 mils). For 750 micron (30 mils) PVC liners, the installed cost is approximately $2.00/sq m.

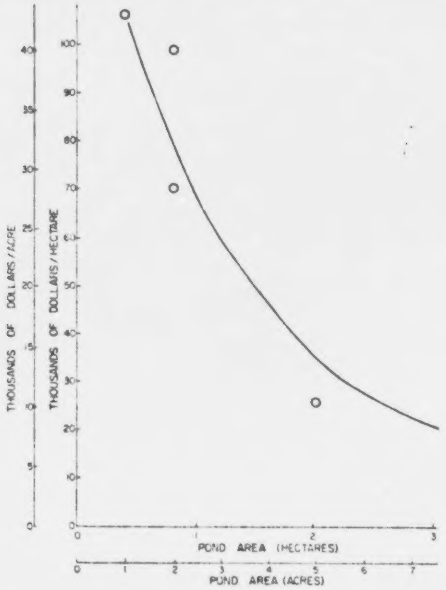

FIGURE 64
CAPITAL COSTS FOR SMALL UNLINED PONDS
(REFERENCE (28), (29), AND (30))

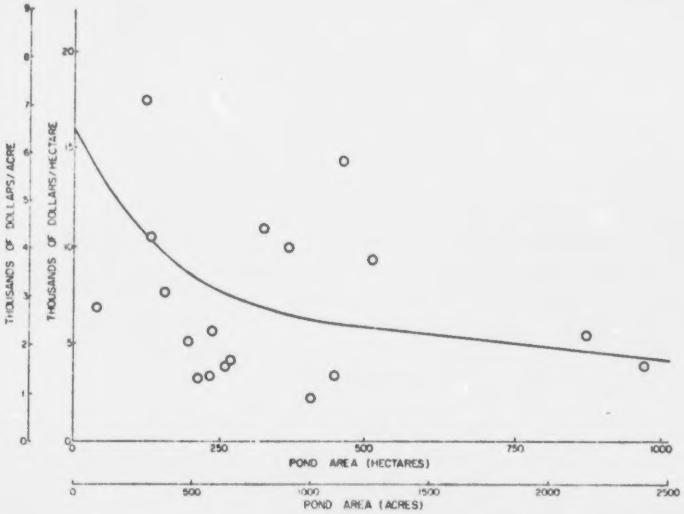

FIGURE 65
CAPITAL COSTS FOR LARGE UNLINED PONDS
(REFERENCE (27))

The construction costs for small lined ponds are given in Figure 66. These values may be conservative as far as film costs are concerned. For large ponds, lined costs have been estimated by adding $2.00/sq m (20¢/sq ft) to the unlined costs. The results are shown in Figure 67.

Since a 200 ha (500 ac) lined pond costs $4 to 6 million this approach for large scale waste treatment and/or storage will require careful investigation before proceeding.

Solar Evaporation Ponds

Table 70 gives the costs for solar ponds as a function of evaporative capacity. Table 71 gives costs per 3785 liters (1000 gallons) calculated from Table 70 for comparison with treatment costs for other processes. A pond and liner life of 20 years was assumed.

Carbon Adsorption

There are a few instances where organic materials are present in the inorganic chemicals industry water wastes. These organic materials may be handled in many cases by conventional biological digestion or they may be treated by methods such as carbon adsorption.

Installation costs range from 5¢ to 20¢/3785 l (1000 gal) treated. A cost of 15¢ was chosen as representative. This cost includes 5 percent loss of efficiency upon carbon regeneration.

Combining capital costs from Figures 68 and operating costs from above, yields overall treatment costs as shown in Figure 69.

Ion Exchange and Demineralization

Ion-exchange and demineralization water treatments are widely used, particularly for pretreatment of boiler, cooling tower, and process feeds.

Ion exchange, as its name implies, replaces undesired ions with less objectionable ones. Some of the ions removed in this way include magnesium, calcium, iron, manganese, carbonate, nitrate, and sulfate. Usually these ions are replaced by sodium or chloride ions. The total quantities of dissolved solids remain almost the same. Demineralizations, on the other hand, by a combination of ion exchange operations, actually remove almost all the dissolved solids.

Ion Exchange Costs

Ion exchange units are generally restricted to treating waste waters with low concentrations of dissolved solids. Two common

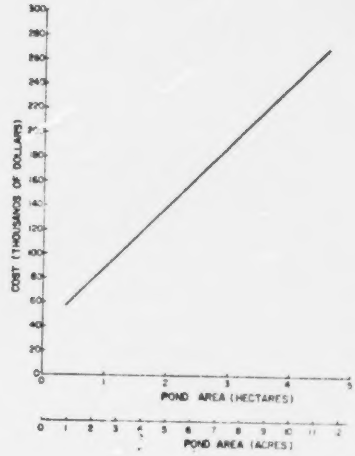

FIGURE 66
CONSTRUCTION COST OF SMALL LINED PONDS
(REFERENCE (30))

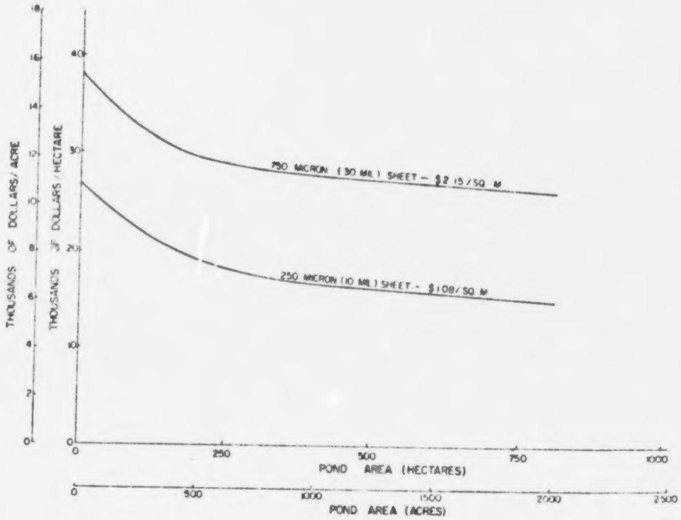

FIGURE 67
CAPITAL COSTS FOR LARGE LINED PONDS

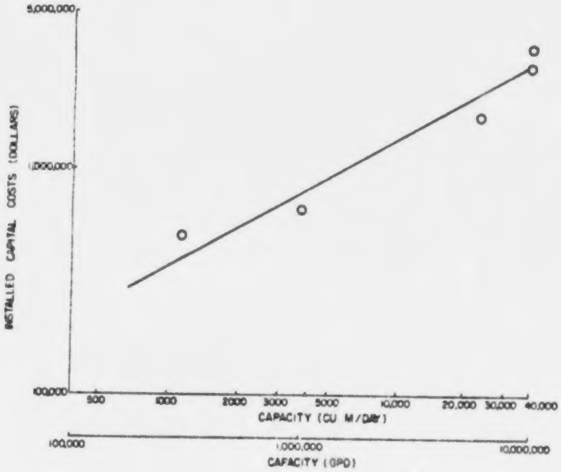

FIGURE 68
INSTALLED CAPITAL COST FOR CARBON ADSORPTION EQUIPMENT

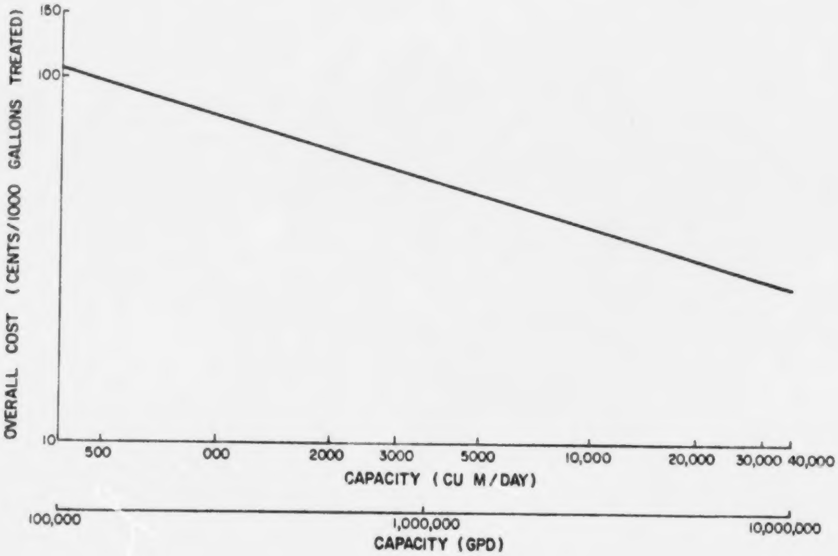

FIGURE 69
OVERALL COSTS FOR CARBON ADSORPTION

TABLE 70. Capital Costs for Lined Solar Evaporation Ponds as a Function of Capacity*

Capacity cu m/day (GPD)	Evaporation--Rainfall Differential 2 Ft. Hectare (Acres)	2 Ft. Capital Costs	4 Ft. Hectare (Acres)	4 Ft. Capital Costs	6 Ft. Hectare (Acres)	6 Ft. Capital Costs
38 (10,000)	2.2 (5.6)	150,000	1.1 (2.8)	95,000	0.8 (1.9)	80,000
189 (50,000)	11.2 (28)	420,000	5.6 (14)	212,000*	3.7 (9.3)	220,000*
378 (100,000)	22 (56)	820,000	11.2 (28)	470,000	7.5 (18.7)	282,000
945 (250,000)	56 (140)	1,960,000	28 (70)	1,010,000	18.7 (46.7)	690,000
1890 (500,000)	112 (280)	3,700,000	56 (140)	1,960,000	37.3 (93.3)	1,350,000
3785 (1,000,000)	220 (560)	6,650,000	112 (280)	3,700,000	74.8 (187)	2,570,000

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*Ponds of 10 acres and under tanke from Figure 74; those over 10 acres taken from Figure 75.

TABLE 71. Costs for Solar Evaporative Pond Disposal

20-Year Pond Life

Evaporative Capacity cu m/day (GPD)	Cost, ¢/3785 liters (¢/1,000 Gal.) Evaporation-Rainfall Differential 2 ft/yr	4 ft/yr	6 ft/yr
38 (10,000)	214	136	114
379 (100,000)	117	67	40
3785 (1,000,000)	95	53	37

treatment methods are: (1) Sodium-hydrogen zeolite dealkalizers (2) Zeolite softeners

Estimated costs of ion-exchange operations as a function of dissolved solids concentration are shown below:

Total Dissolved Solids (mg/l)	Zeolite Softening, ¢/3785 l (¢/1000 gal)	Sodium-Hydrogen Dealkalizer, ¢/3785 l (¢/1000 gal)
200	5.7	6.4
500	10.8	9.5
750	15.0	12.2

While these values are only approximations, they do show that zeolite "softening" or ion exchange with sodium chloride or sodium chloride plus sulfuric acid is fairly low in cost even at the 750 mg/l total dissolved solids level. Ion exchange does not remove dissolved solids from waste water. Therefore, ion exchange units produce regenerant wastes which require disposal. With these considerations, ion exchange units are generally used only for certain specific harmful ion situations.

Demineralization Costs

The cost of demineralization equipment itself is fairly consistent for the low solids fixed bed units used for most applications. For the specialty systems described in Section VII, particularly at solids concentrations above 1000 mg/l, the costs are significantly higher for a given capacity. Both the special nature of these units and the influence of the higher resin volumes required to take the increased loading increase capital costs. Installed capital costs can also differ greatly depending on land availability, pretreatment facilities needed, buildings, storage tanks, and engineering and contractor costs. The installed capital costs developed in this section have been adjusted using 33 percent of equipment costs for installation and six percent increase per year in equipment costs. All values are in 1973 dollars. They do not include resin costs which are covered in operating costs. Values for capital costs were taken from literature references. Average values are plotted in Figure 70.

Generally, installed capital costs for conventional demineralization units are about one-half the cost for reverse osmosis installations with similar capacities.

The operating costs for demineralizations are made up of the costs of: (1) Resin; (2) Chemicals; (3) Labor and Maintenance.

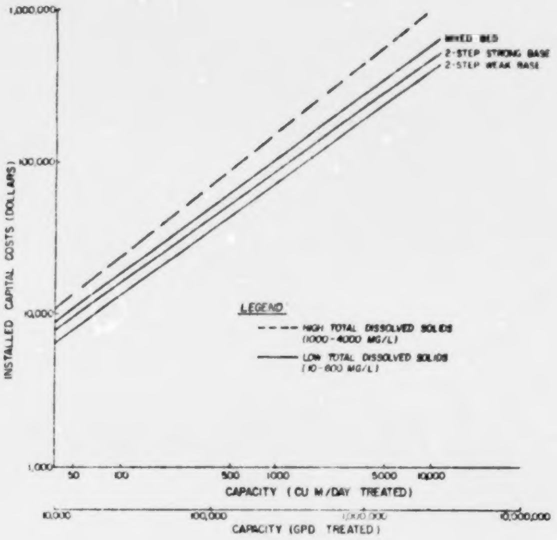

FIGURE 70
INSTALLED CAPITAL COST vs. CAPACITY
FOR DEMINERALIZATION

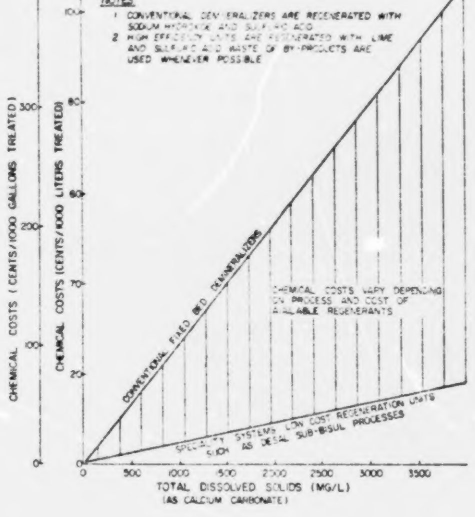

FIGURE 71
CHEMICAL COSTS FOR DEMINERALIZATION

For the higher dissolved solids levels, chemical costs are the primary expense. These costs are shown in Figure 71. Overall costs are given in Tables 72 and 73.

Reverse Osmosis Treatment Costs

The costs involved with waste treatment using reverse osmosis are given comprehensive coverage in reference (49). The costs for reverse osmosis treatment include capital equipment, membrane replacement, pretreatment, power and labor plus maintenance materials.

The capital costs for reverse osmosis installations vary with plant size. Small units cost $1.00 to $1.50 per 3.78 l/day (gal/day) while large units lower this cost to $0.50 or less per 3.78 l/day as shown in Figures 72 and 73. These costs do not include either extensive pretreatment or disposal facilities.

The selection of the membrane material, either sheet or hollow fiber, is governed by the nature of the waste to be treated and the product water quality desired. In general, tighter (small pore size) membranes have lower flux rates than more open structured ones. Therefore, to obtain low total dissolved solids product water, the area required for treatment will be significantly higher than for an allowable high total dissolved solids product water. In turn, the increased membrane surface area will increase the capital and membrane replacement costs. This correlation is shown in Figure 74.

Membrane life is one of the major factors of operating costs. Currently membrane life appears to be one to three years, with the average shifted toward the one to two year interval for replacement. This short and variable life has restricted use of reverse osmosis in many otherwise logical applications.

Since modules constitute one-third to one-half of the capital equipment costs, the life of the modules is critical. Unfortunately, module performance and life are difficult features to predict and control. For this reason, cost developments in this section are based on a two year life. As application experience increases, improved membrane life will significantly reduce operating costs. Table 74 summarizes membrane replacement costs for a membrane life of two to three years.

Various chemical pretreatments are required to prepare feedwater for passage through the membrane units. Included in these pretreatments are pH adjustment, such as acid addition to eliminate carbonate scaling, sulfate scaling control through addition of sodium hexametaphosphate, and chlorination for organics.

TABLE 72 . Overall Costs for Demineralization

FIXED BED 2-STEP DEMINERALIZATION

Capacity Treated cu m/day(GPD)	Installed Capital Amortization ¢/1000 gallons or 3785 liters	Resin Costs ¢/1000 gallons or 3785 liters	Chemical Costs ¢/1000 gallons or 3785 liters	Labor and Maintenance Costs ¢/1000 gallons or 3785 liters	Overall Costs ¢/1000 gallons or 3785 liters
		100 mg/liter, Total Dissolved Solids			
38(10,000)	26.3	3.2	10	1.8	41.3
378(100,000)	16.3	3.2	10	1.1	30.6
3785(1,000,000)	8.2	3.2	10	0.5	21.9
		500 mg/liter, Total Dissolved Solids			
38(10,000)	26.3	3.2	50	1.8	81.3
378(100,000)	16.3	3.2	50	1.1	70.6
3785(1,000,000)	8.2	3.2	50	0.5	61.9
		1000 mg/liter, Total Dissolved Solids			
38(10,000)	26.3	3.2	100	1.8	131.3
378(100,000)	16.3	3.2	100	1.1	120.6
3785(1,000,000)	8.2	3.2	100	0.5	111.9
		2000 mg/liter, Total Dissolved Solids			
38(10,000)	26.3	6.4*	200	1.8	234.5
378(100,000)	16.3	6.4*	200	1.1	223.8
3785(1,000,000)	8.2	6.4*	200	0.5	215.1

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*Double resin cost assumed for increased loading.

TABLE 73. Overall Costs for Demineralization

SPECIALTY PROCESSES -- High Efficiency-Low Cost Regeneration Units

Capacity Treated cu m/day(GPD)	Capital Amortization ¢/1000 gallons or 3785 liters	Resin Costs ¢/1000 gallons or 3785 liters	Chemical Costs ¢/1000 gallons or 3785 liters	Labor Maintenance Costs ¢/1000 gallons or 3785 liters	Overall Costs ¢/1000 gallons or 3785 liters
		1000 mg/l , Total Dissolved Solids			
38(10,000)	43	3.2	17	2.9	66.1
379(100,000)	21.4	3.2	17	1.4	43.0
3785(1,000,000)	12.5	3.2	17	0.8	33.5
		2000 mg/l , Total Dissolved Solids			
38(10,000)	43	6.4*	33	2.9	85.3
379(100,000)	21.4	6.4*	33	1.4	62.2
3785(1,000,000)	12.5	6.4*	33	0.8	52.7
		3500 mg/l , Total Dissolved Solids			
38(10,000)	43	12.8**	60	2.9	118.7
379(100,000)	21.4	12.8**	60	1.4	95.6
3785(1,000,000)	12.5	12.8**	60	0.8	86.1

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*Double resin cost assumed for increased loading.

**Four times low solids resin costs assumed for this very heavy loading.

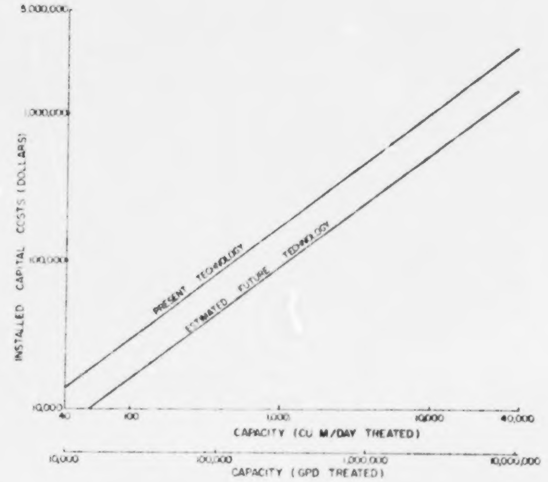

FIGURE 72
INSTALLED CAPITAL COSTS FOR
REVERSE OSMOSIS EQUIPMENT

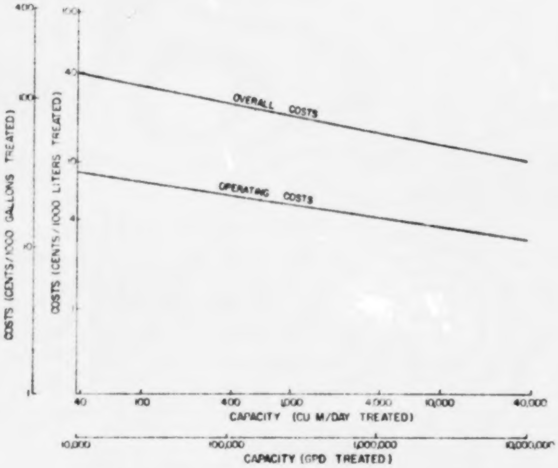

FIGURE 73
COSTS FOR REVERSE OSMOSIS TREATMENT

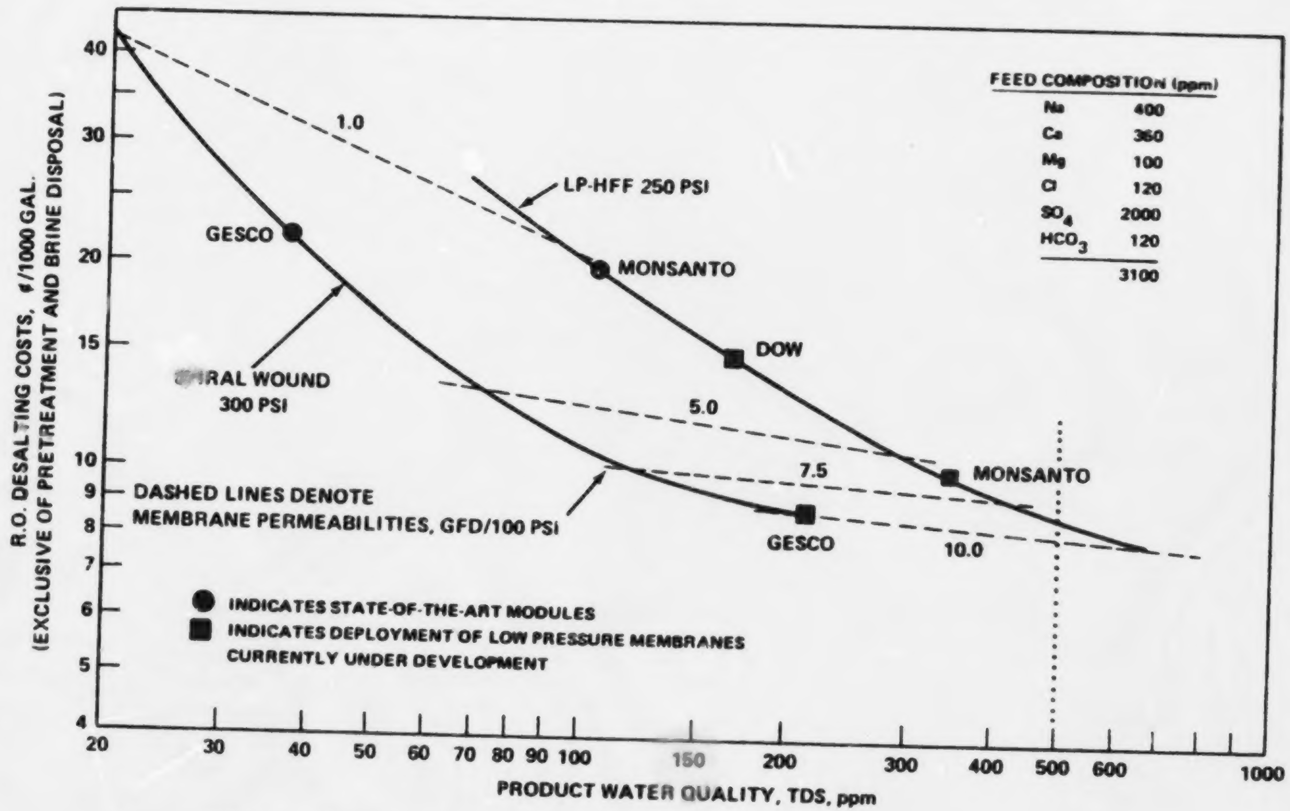

FIGURE 74 TRADE-OFF BETWEEN MEMBRANE PERMEABILITY (FLUX) AND SELECTIVITY (REJECTION AND PRODUCT WATER QUALITY) FOR CELLULOSE ACETATE BASE MEMBRANES (10 MGD PLANT @ 55% RECOVERY, 3100 ppm TDS FEED)

TABLE 74. Reverse Osmosis -- Membrane Replacement Costs

Volume Treated		¢/1000 gal. or 3785 l Treated			
		2 Yr. Life		3 Yr. Life	
cu m/day	GPD	Present	Future	Present	Future
38	10,000	45	22	30	15
95	25,000	45	22	30	15
189	50,000	45	22	30	15
379	100,000	38	20	25	13
945	250,000	38	20	25	13
1,890	500,000	30	15	20	10
3,785	1,000,000	30	15	20	10
18,900	5,000,000	22	12	15	8
37,850	10,000,000	15	8	10	5

Taken from Reference (49), p. 108. Converted to cu m/day and GPD treated basis plus two (2) year life adjustment.

TABLE 75. Reverse Osmosis -- Operating Costs

Volume Treated		¢/1000 gal. or 3785 l Treated			
cu m/day	GPD	Power*	Chemicals**	Labor Plus Maintenance Materials	Total Cost
38	10,000	6	4	28	38
95	25,000	6	4	20	30
189	50,000	6	4	15	25
379	100,000	6	4	10	20
945	250,000	6	4	7	17
1,890	500,000	6	4	5	15
3,785	1,000,000	6	4	4	14
18,900	5,000,000	6	4	2	12
37,850	10,000,000	6	4	15	11.5

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*At 1¢ per kwhr.

**Will vary depending on pretreatment required.

***Additional breakdowns in reference cited above.

A low energy requirement is one of the major advantages of the reverse osmosis process. The primary energy requirement is for high pressure pumps.

The operating costs are summarized in Table 75. Figure 73 combines the information developed into overall reverse osmosis treatment costs. These values are based on conservative engineering and industrial calculations and assumptions, assuming straight line ten year depreciation, six percent money and membrane life of two years.

Evaporation Costs

Although there are many different designs and variations of evaporative equipment, four basic types, as described in Section VII, are commonly employed in the inorganic chemicals manufacturing industry. They are: (1) single-effect evaporators; (2) multi-effect evaporators; (3) high efficiency vertical tube and multi-effect flash evaporators; and (4) low energy specialty evaporators. Costs for these types of equipment and their operation are given in the following subsections.

Each type of evaporator has its individual operating specifications, as shown in Table 76. Figure 75 compares the energy requirements of each evaporator type with other treatment techniques as a function of dissolved solids concentration.

The selection of evaporative equipment depends on the job requirements. For high volume, low solids stream concentrations the VTE, or multi-flash type units should be used. Ninety percent or more of the water can be recovered as high purity product with relatively low energy requirements. The remaining five to ten percent can be more economically removed by recirculating evaporators or dryers. Although energy requirements are high per kg of water removed for single effect evaporators and dryers, the total energy requirement and capital costs for this step are relatively low. High volume, high solids content streams may be handled similarly except that conventional multi-effect evaporators should be used for the first concentration.

Low Energy Specialty Evaporator Costs

Capital costs for a low energy specialty unit, the flat plate vapor compression evaporator, are given below.

Capacity cu m/day (gal/day)	Installed Capital Costs, $
379 (100,000)	635,000
850 (225,000)	1,350,000
1890 (500,000)	2,500,000

TABLE 76. Evaporator Characteristics

Characteristics	Recirculative Evaporator	Multi-effect	High Efficiency Vertical Tube Evaporator	Low Energy Specialty Evaporator
Effects	1-3	2-6	10-20	15-30
Evaporative energy, kg cal/kg (Btu/lb)	222-555 (400-1000)	100-333 (180-600)	42-56 (75-100)	19-56 (35-100)
Optimun concentration range, % by weight of solids	20 to max.	10-50	1-10	1-10
Ability to handle heavy crystallizing or suspended solids load	Excellent	Good, can be easily equipped for recirculation	Poor, not operable	Good, for calcium sulfate and other slurries
Optimum capacity range	Best for small capacity below 5000 GPD	Good over wide capacity range 10,000-2,000,000 GPD	Mainly for high capacity more than 1,000,000 GPD	Mainly for high capacity more than 100,000 GPD
General costs	Relatively low	Intermediate	High	Highest

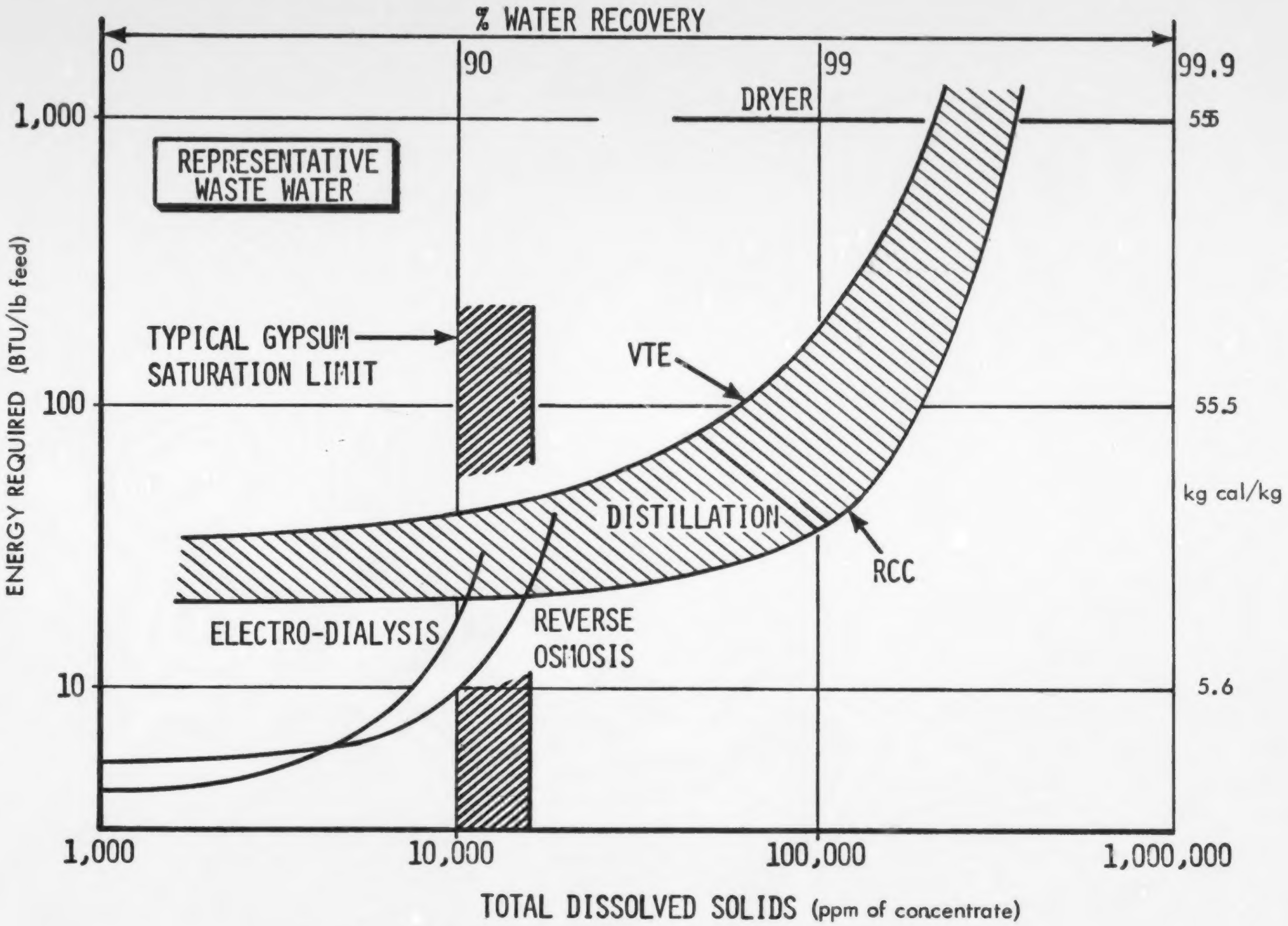


FIGURE 75. ENERGY COMPARISON FOR DISSOLVED SOLIDS REMOVAL

Larger capacities are made up of multiple small units. Operating expenses include costs for electric power, pretreatment chemicals, and labor.

Unlike most evaporators, this unit uses an electrically driven compressor instead of steam for its energy. Therefore, operating cost is directly influenced by the electrical power costs in the area. This cost may range from $0.003/kwhr to over $0.01/kwhr. For industrial applications, operating power costs are taken as $0.01/kwhr. The amount of power required depends on the specific operating conditions. The following table gives estimated power as a function of the concentration of total dissolved solids in the concentrate.

Concentrate TDS* (mg/l)	kwhr/1,000 gal or 3785 l Treated
10,000	60
50,000	65
100,000	100
200,000	250

---

*Total solids, including those suspended in the slurry, may be several times greater than the dissolved solids.

Operating and overall costs in ¢/3785 liters (1000 gallons) for an 850 cu m/day (225,000 gpd) unit are given below:

Concentrate TDS*, mg/l	Power ¢/3785 l (¢/1000 gal)	Chemicals ¢/3785 l (¢/1000 gal)	Operation and Maintenance ¢/3785 l (¢/1000 gal)	Total ¢/3785 l (¢/1000 gal)
10,000	60	3	52	115
50,000	65	3	52	120
100,000	100	3	52	155
200,000	250	3	52	305

---

*Since sparingly soluble water contaminants such as calcium sulfate and silica precipitate with concentration, total solids are usually much higher.

Concentrate TDS mg/l	Capital ¢/1,000 gal or 3785 l	Operation ¢/1,000 gal or 3785 l	Total ¢/1,000 gal or 3785 l
10,000	257	115	327
50,000	257	120	377
100,000	257	155	412
200,000	257	305	562

These overall cost values are consistent with the basis used for other calculations of this report -- industrial 10 year depreciations and higher cost electric power than would be available to many current users. Low cost power and 35 year capital writeoffs would bring the overall costs down to approximately $2.00/1,000 gallons or 3785 l treated.

It should also be emphasized that the power requirement correlation with total dissolved solids neglects the suspended solids portion of the recirculated slurry. Since many dissolved solids such as calcium sulfate are only sparingly soluble in water, concentration causes them to precipitate and form slurries. The unit is designed to handle such slurries up to total solids contents of 35 to 50 percent (at which point the total dissolved solids might be one percent or 10,000 mg/l). The critical difference here is that dissolved solids raise the boiling point of the solution, whereas suspended solids do not. The ability to handle slurries is one of the key technology advantages over multi-flash and vertical tube evaporators which are discussed next.

Vertical tube, multi-stage flash, and other high efficiency evaporators have been used in units to recover pure water from salt or brackish sources. Installed capital costs are shown in Figure 76 and operating and overall costs are given in Figure 77.

Conventional Multi-Effect Evaporators

For the heavy-duty, very high solids evaporations, industrial type multi-effect evaporators are commonly used. The inorganic salts in sea water and inorganic chemical industry are very corrosive. Even cupro-nickel and stainless steel alloys may not be sufficient for many of the solutions involved. Therefore, for this section, costs are given for solid nickel, titanium and tantalum materials, as well as stainless steel. Nickel construction raises the cost significantly, but will provide the reliable service required for industrial applications.

In selecting the optimum number of effects, a balance has to be made between equipment costs and operating costs. If the addition of an effect will not pay for itself in lower steam costs within approximately three years, the effect will probably not be added. It is rare that more than six or seven effects can be justified in this manner. (This is particularly true because of the high dissolved solid solutions or waste involved). Figures 78 and 79 show the interrelationships between number of effects and capital cost and steam usage, respectively.

Capital costs may be calculated rather quickly and directly from Figure 80:

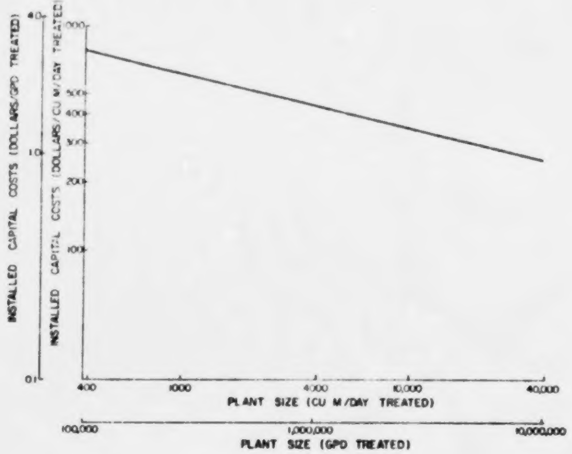


FIGURE 76
INSTALLED CAPITAL COSTS vs. CAPACITY FOR HIGH EFFICIENCY VTE OR MULTI-STAGE FLASH EVAPORATORS

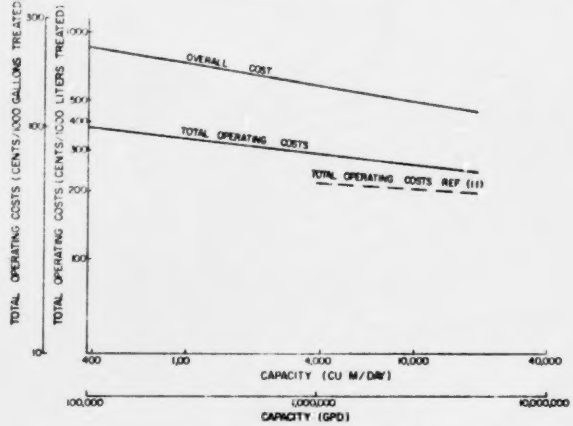
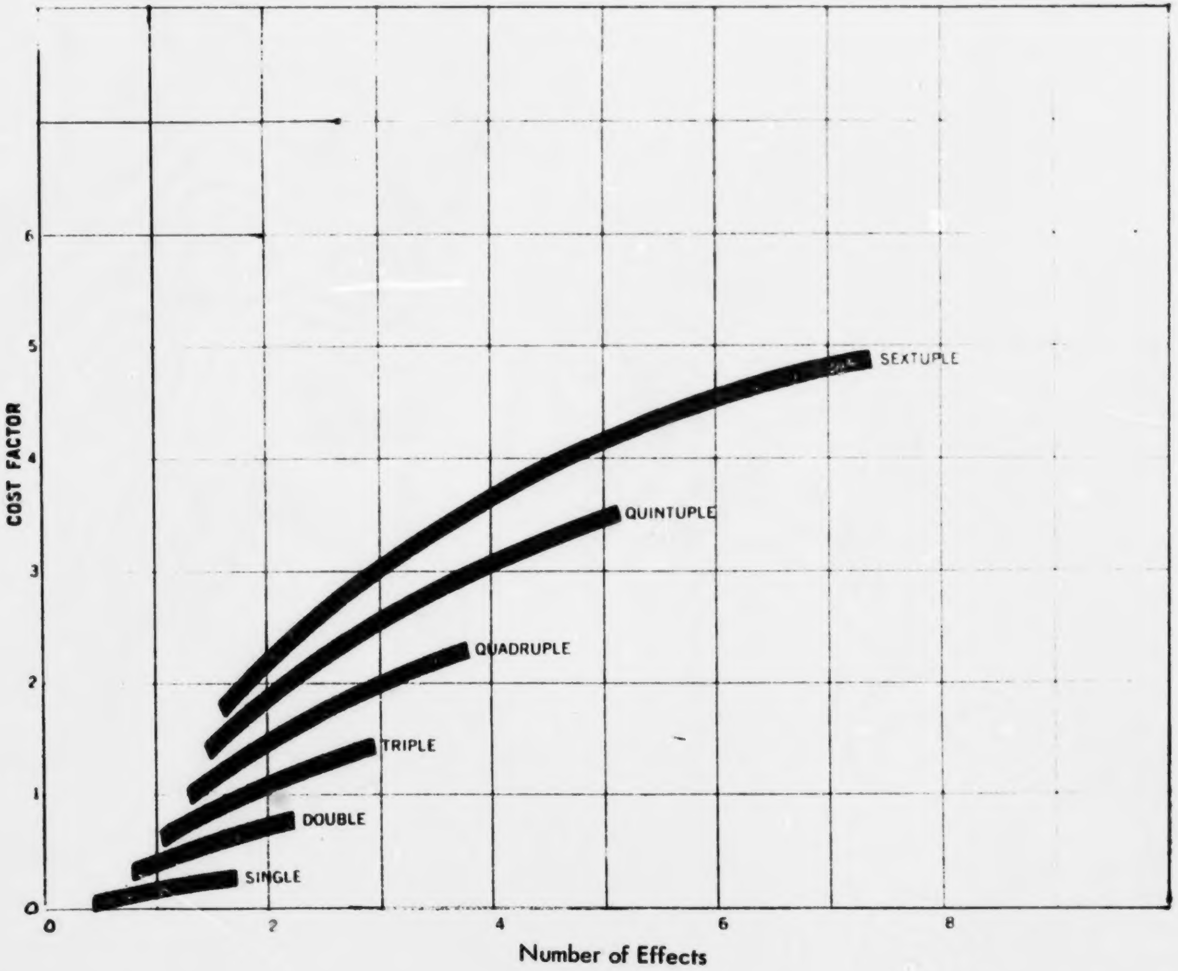
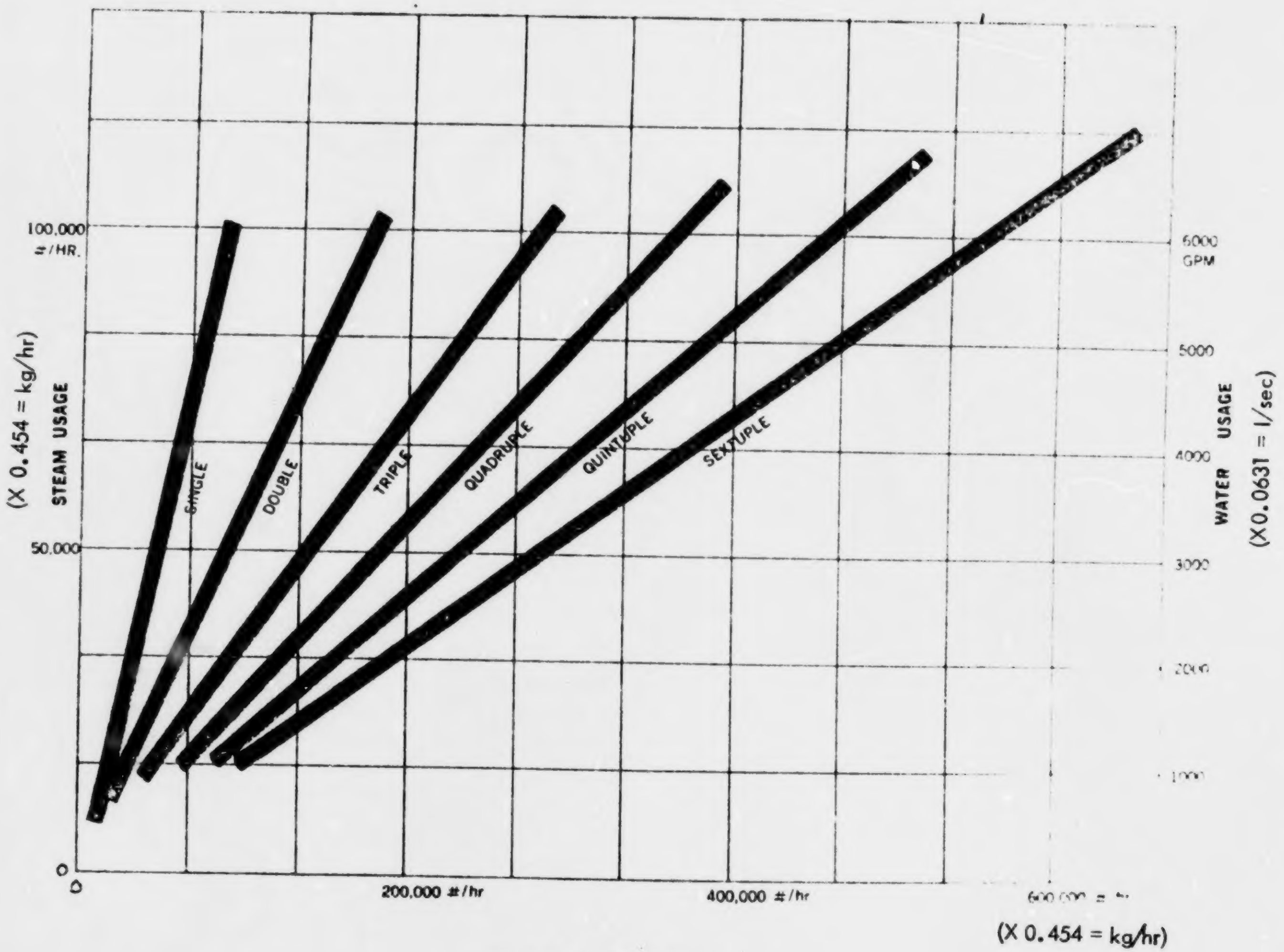


FIGURE 77
OVERALL AND TOTAL OPERATING COSTS FOR VTE AND MULTI-FLASH EVAPORATORS



EVAPORATION

Figure 78. Capital Costs Vs. Effects for Conventional Multi-Effect Evaporators.



EVAPORATION

Figure 79. Steam Usage Vs. Effects for Conventional Multi-Effect Evaporators

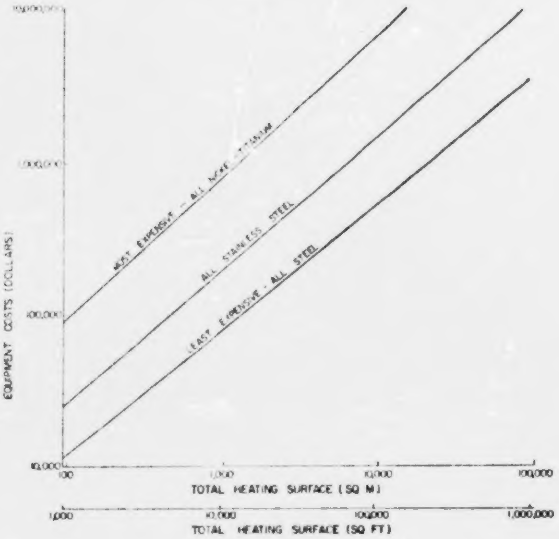


FIGURE 80
CORRELATIONS OF EQUIPMENT COST WITH EVAPORATOR HEATING SURFACE

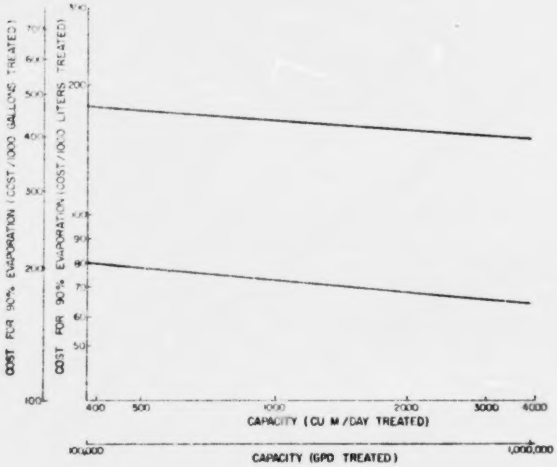


FIGURE 81
OVERALL COSTS FOR 6-EFFECT EVAPORATOR TREATMENT OF WASTE WATER

Volume Treated cu m/day (gal/day)	Total Installed Capital Cost, $
378 (100,000)	667,000
945 (250,000)	1,530,000
1890 (500,000)	2,800,000
3785 (1,000,000)	5,470,000

Analogous values for stainless steel and other construction material capital costs may be similarly derived.

Operating costs include steam costs and labor and maintenance. Chemical pretreatment costs are usually minimal. Operating costs are summarized below for six-effect evaporators.

Overall costs for all-nickel and stainless steel six-effect evaporators are given in Figure 81.

Volume Treated cu m/day	Volume Treated gal/day	Steam Costs in ¢/3785 l (¢/1000 gal)	Labor and Maintenance ¢/3785 l (¢/1000 gal)	Total Costs ¢/3785 l (¢/1000 gal)
378	100,000	95	91	186
945	250,000	95	80	175
1890	500,000	95	71	166
3785	1,000,000	95	68	163

Single-Effect Evaporators

When evaporation loads are small as for final concentrations or minor waste streams, evaporative energy costs are secondary. In these cases, equipment costs and reliability of operation are the controlling considerations. Various designs are available for handling crystallizing solids or slurries and design and industrial technology is widely available.

Using Figure 80 and following the same procedures and costs for energy, installation, maintenance and labor as for multieffect evaporators, costs can be developed. Essentially, costs for single-effect evaporators are treated as an extrapolation of the multi-effect cost values. A summary of the costs involved is shown below for single-effect evaporators assuming stainless steel construction.

Treated cu m/day	Treated gal/day	Installed Capital Costs, $	Capital Writeoff ¢/3785 l (¢/1000 gal)	Operating Costs ¢/3785 l (¢/1000 gal)	Overall Costs ¢/3785 l (¢/1000 gal)
38	10,000	8,000	34	564	598

189	50,000	28,000	24	551	575
379	100,000	45,000	19	545	564
945	250,000	80,000	14	539	553
1890	500,000	146,000	12	536	548
3785	1,000,000	267,000	11	533	544

Basis:

Treated		Installation Costs Percent of	Labor Costs
cu m/day	gal/day	equipment capital	¢/3785 l (¢/1000 gal)
38	10,000	100	30
189	50,000	100	20
379	100,000	50	17
945	250,000	33	10
1890	500,000	33	8
3785	1,000,000	33	5

15 percent Capital writeoff/yr.
4 percent Capital cost/yr for maintenance materials.
90 percent Evaporation.
Steam cost -- $0.70/1000 lbs or $0.70/454 kg.

Similar values for all nickel, titanium or tantalum construction are:

Treated Volume cu m/day	Treated Volume gal/day	Installed Capital Costs,$	Capital Writeoff ¢/3785 l (¢/1000 gal)	Total Operating Costs ¢/3785 l (¢/1000 gal)	Overall Costs ¢/3785 l (¢/1000 gal)
38	10,000	16,000	69	574	643
189	50,000	68,000	58	561	619
378	100,000	133,000	57	555	612
945	250,000	300,000	52	549	601
1890	500,000	532,000	46	545	591
3785	1,000,000	1,060,000	45	542	587

Basis: Same as previously shown except 33 percent of capital costs are used for installation estimates for all capacities.

These figures show that single-effect evaporation costs are largely for steam, with capital costs being only a small fraction of the overall cost. All nickel, titanium, tantalum or other high cost materials of construction are often needed and can be economically used.

The high overall costs per liter treated also indicate that single-stage evaporators are restricted to small capacities. For example, at the 3785 cm/day (1,000,000 gal/day) capacity, yearly overall cost for stainless steel equipment is $1,910,000. Comparable multi-effect and VTE costs are $583,000 to $1,400,000 yearly. Obviously the higher efficiency units would be used whenever possible. At the 379 cu m/day (100,000 gal/day) level, comparable costs are $198,000/yr for single-effect, $72,200/yr for six-effect, and $78,500/yr for 14-effect. For this case, there is still approximately $120,000/yr savings in going to multi-effect evaporators. Single-effect evaporators would normally be used in the capacity range of 48 cu m/day (10,000 gal/day).

Mechanical Drying Costs

The crystallized, suspended or dissolved solids removed in the previous evaporation section can either be recycled, sold, or disposed of in their concentrated form. In some cases, they may require further treatment. Whenever possible, suspended solids should be dewatered by centrifuging or filtration. These relatively low cost treatments may be all that is needed, or reduction to full dryness may be required. When full dryness is required, the filter cakes, centrifuged solids, and concentrated solids may be subjected to conventional thermal drying. Heating may be by gas, oil, or steam. Types of dryers include rotary drum dryers, screw type mechanical dryers, scraped surface tunnel dryers and heated evaporation pans.

Capital costs and labor costs are minimal in comparison to energy costs. Labor and materials are estimated to cost $0.11 to $0.33/kkg ($0.10 to $0.30/ton) of product for small dryers (Reference (71).

Taking energy costs as $0.50 per 252,000 kg cal (million BTU) (gas or oil combustion) and an energy utilization efficiency of 50 percent, drying costs are $1.00/454 kg (1000 lb) of water evaporated.

Drying costs as a function of solids content are given below:

Percent Solids in Feed by weight	Drying Costs, ¢/454 kg (¢/10,000 lb)	Drying Costs, ¢/3758 l (¢/1000 gal)
90	10	Dry Basis
80	20	Dry Basis
70	30	Dry Basis
60	40	Dry Basis
50	50	420
40	60	500
30	70	580
20	80	600

Aside from the energy costs involved, there are practical drying problems with common dissolved salts such as calcium chloride, potassium chloride, and magnesium chloride. These can be dried but they hold tenaciously to residual water and must be given special handling techniques including the use of drum flakers or pan evaporators.

Deep Welling Costs

The capital costs for injection wells vary greatly, from $40,000 to more than $1,000,000. The costs depend on factors such as well depth, geology, well hole size, care in drilling, well construction, geographical location, pretreatment requirements, instrumentation and monitoring, corrosion problems, injection pressure, and maintenance. The operating life of such wells is difficult to predict and may be very short due to blockage, contamination of water aquifiers, or other reasons.

The principal cost factors in well construction are drilling contractor costs and casing and tubing costs. These two factors comprise approximately two-thirds of the total construction costs. The larger and deeper the hole, the higher the contractor costs will be.

Surface equipment such as pumps, filters, tank, piping, and instrumentation can vary from 50 percent of construction costs to 100 percent or more. Injection pressures above 27 atmospheres (400 psi) require more expensive pumps. Corrosive liquids require more expensive materials in the liquid handling equipment.

The average deep well capital and operating costs determined from a recent comprehensive survey (Reference (77) are: capital cost -- $305,000; operating costs -- 30¢/3785 l (1000 gal).

Operating costs for deep well disposal range from 4¢/3785 l (1000 gal) to $2.20/3785 l (1000 gal). The lower costs are for shallow wells, low injection pressures, minimum pretreatment, relatively low corrosiveness, and a minimum of monitoring and instrumentation. The higher operating costs involve deep wells with high injection pressures, extensive pretreatment, high maintenance costs, extensive monitoring and instrumentation, and corrosion resistant equipment. In any cost calculations involving deep wells, as discussed in Section VII, either a backup well or alternate disposal facility is necessary. This will increase the average capital cost to approximately $500,000 (for a single-well operation).

Calculating overall costs for deep well disposal at a 1890 cu m/day (500,000 gal/day) rate and using a 15 percent capital amortization yields an overall cost of 73¢/3785 l (1000 gal).

Solids Wastes Disposal Costs

The slurries, water soluble solids and water insoluble solids obtained from control and treatment of inorganic chemicals industry water-borne wastes have to be contained, or disposed of, in a safe and economical manner.

Provided that the solids are insoluble in water, most solid wastes from the inorganic chemicals industry may be land dumped or land-filled. Costs are $0.22 to $0.66/kkg ($0.20 to $0.60/ton) of solids -- for simple dumping or landfilling. Figure 82 gives a breakdown of complete landfilling costs. Large scale operations without cover cost less than $1.11/kkg ($1.00/ton). If cover is involved for appearance or zoning requirements, the costs may increase to $1.05 to $2.20/kkg ($1.50 tc $2.00/ton).

If the evaporation-rainfall situation for the disposal area is favorable (as is the case for much of the southwestern U.S. and some other areas of the country), then landfill in an impervious, lined pan is feasible for soluble solids. Operation costs are similar to those for landfill with no cover, $0.22 to $0.66/kkg ($0.20 to $0.60/ton).

Landfilling of containerized soluble solids in plastic drums or sealed envelopes is practicable but expensive. Blow-molded plastic drums, made from scrap plastic (which is one of the present major problems in solid waste disposal) could be produced for $11-22/kkg ($10-20/ton) capacity at 227 kg (500 lb) solids per drum and a rough estimate of $2.50-5.00 cost/drum. A more economical method, particularly for large volumes, would be sealed plastic envelopes, 750 microns (30 mils) thick.

At $1.10/kg ($.50/lb) of film, low density polyethylene costs about 10¢ per 0.0929 sq m (1 sq ft). Using the film as trench liner in a 1.8 m (6 ft) deep trench 1.8 m (6/ft) wide, the perimeter (allowing for overlap) would be approximately 7.5 meters (25 feet). At a density of 1.6 gm/cc (100 lb/cu ft) for the solid, costs of plastic sheet/kkg would be $2.00 ($1.75/ton). With sealing, the plastic envelope cost would be approximately $2.20/kkg ($2/ton). With landfill costs of $2.20/kkg ($2/ton) additional, the total landfill disposal costs would be about $4.40/kkg ($4/ton).

The above figures for soluble disposal using plastic containers, bags or envelopes are only rough estimates. Also, the technology would not be suitable for harmful solids or in situations where leaching contamination is critical.

Treatment Costs for Ancillary Water-Borne Wastes

In many plants of this study ancillary wastes such as boiler blowdowns, cooling tower blowdowns, ion exchange regenerants, and contributions from air purification equipment, are either the sole or dominant contributors to water-borne wastes coming from the plant. Rarely is removing these wastes from plant effluent

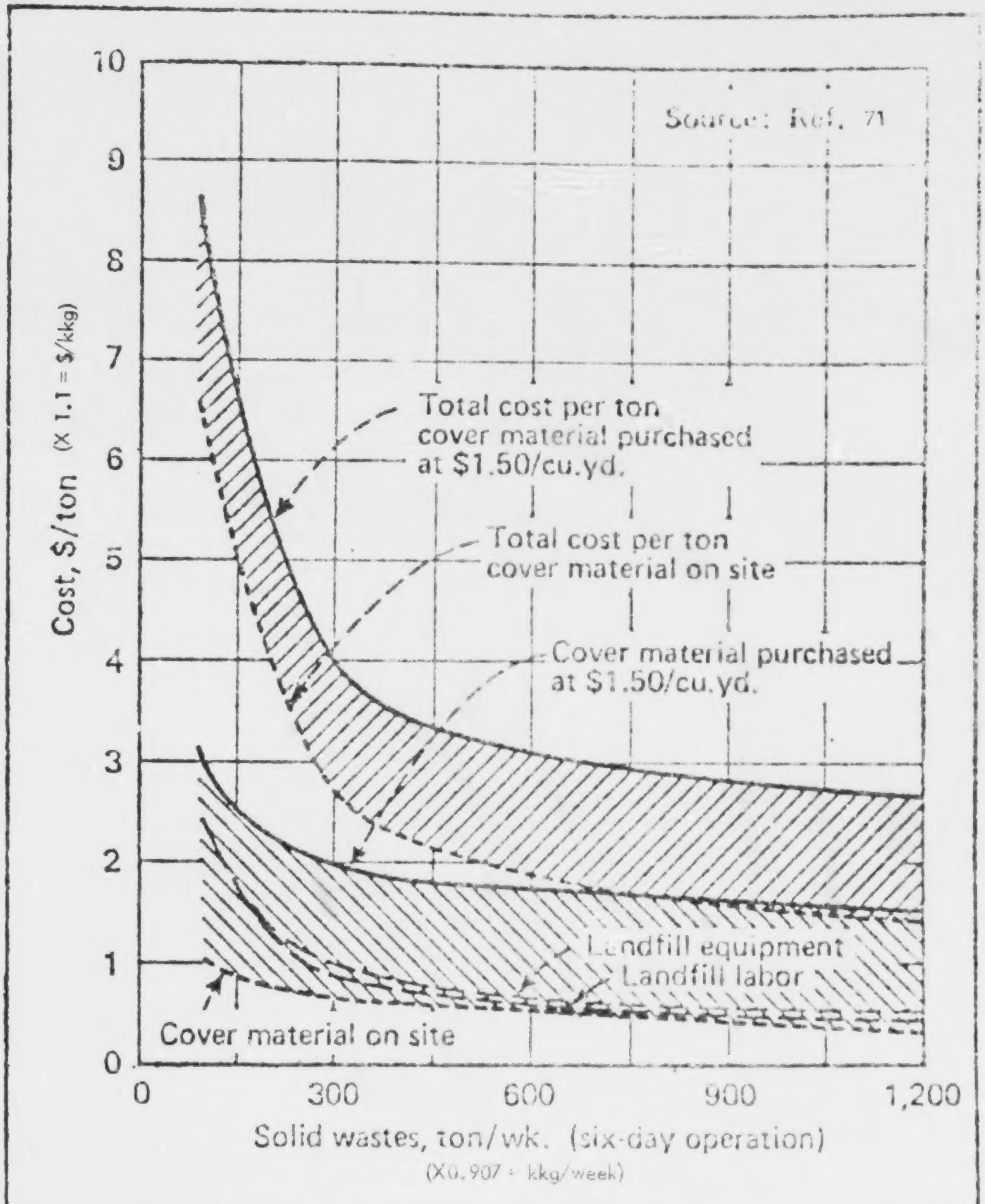


Figure 82. Disposal Costs for Sanitary Landfills

water considered part of the treatment of waste abatement process costs.

Air-Borne Waste Abatement Costs

Five chemicals of this study have been selected for specific cost analysis. They are described below.

Sulfuric Acid

Reduction of sulfur dioxide in the stack gas of sulfuric acid plants to specified limits is expensive for most existing plants. In each of two plants of this study (113 and 023), over $2,500,000 has been spent for this purpose alone. As regulations tighten, other plants will have to be modified similarly. The nature of these modifications should be determined by the overall costs and performance of the sulfur dioxide unit considered.

If a sulfuric acid producer does not choose to follow the path of scrubbing sulfur dioxide from the stack gases, it will undoubtedly be more profitable to recycle sulfur dioxide which should have a recovered sales value of approximately $50/kkg ($45/ton) and eliminate the expense of sodium hydroxide or other chemicals.

Both add-on double adsorption systems and other processes which have no water-borne wastes exist. New plants all use the double adsorption processes.

Calcium Oxide and Calcium Hydroxide

The manufacturing process for calcium oxide and calcium hydroxide has no waste water. The only contribution is from stack scrubbers which collect the lime dust in water.

Current practice is to settle out solids from the scrubber water in ponds and possibly neutralize this effluent before discharge to surface water. Plant 057 currently follows this general type of procedure and plans to install a cyclone recovery and calcining unit on the waste stream at a cost of $750,000. Cost of installation will be covered by product value obtained. This will remove almost 100 percent of the suspended solids. Some dissolved solids remain. Calcium oxide is soluble to the extent of about 1000 mg/l. The water may be recycled for closed loop scrubbing.

A second approach, which escapes water-borne waste and waste recovery problems, is dry bag collection. The exemplary plant of this study has no water effluent and uses dry bag collection systems. Installation cost was $675,000 with annual operating costs of $37,500.

Calcium Carbide

There is no water-borne process waste from the calcium carbide manufacturing process. The only contributions are ancillary wastes -- cooling tower blowdowns, ion exchange regenerants and gas stream scrubbings.

For water scrubbers, the water effluent may be isolated, suspended solids removed by ponding or chemical treatment, alkalinity neutralized and a closed loop recycle instituted to avoid dissolved solids discharge. Capital costs for a large plant adjusted to 1973 prices are approximately $750,000 for the scrubber system, $112,000 for improvements, plus a thickener and settling ponds that will bring the total cost up to $1,000,000. Recycle is possible but would require equipment modification. Therefore, over $1,000,000 investment is needed to water-scrub without waterborne waste with both capital and operating costs being losses.

In contrast, one plant of this study uses dry bag collection techniques throughout. Collection and reuse of 10 percent of the raw materials from these dust collectors makes installation profitable, and there are no water-borne wastes involved.

Chlorine

In contrast to the dusts from the first three processes discussed, chlorine is a reactive and noxious gas. It is soluble in water and forms hypochlorites with water or basic materials present such as sodium hydroxide or calcium hydroxide.

The hypochlorites are bleaches and may be sold. They are also reactive and can be used in the treatment of other chemical wastes such as cyanides. This is done in plant 096. Sodium hypochlorite may also be catalytically decomposed and reused. Discharge must be avoided to attain the effluent reduction possible through the application of the best available technology economically achievable. Removal later from the waste stream will be expensive.

Another method for direct utilization of tail gas chlorine is direct burning with hydrogen to produce hydrochloric acid. Plant 057 is planning this approach at an estimated capital investment of $430,000. Return on investment looks good from the standpoint of product value and decreased sodium hydroxide usage.

Aluminum Chloride

The aluminum chloride process has no water-borne wastes, but condenser gas scrubbing removes residual chlorine gas and entrained aluminum chloride fumes. Two exemplary plants (152 and 125) of this study avoid any water-borne wastes as discussed in

Section VII. Costs for a generalized treatment process are shown below to illustrate the dollar values involved. For a discharge of 4.5 kg (10 pounds) of aluminum chloride and 2.25 kg (5 lb) of chlorine per 0.907 kkg (ton) of product in a 18 kkg/day (20 ton/day) plant, treatment costs are developed below for neutralization with sodium hydroxide. Sodium hydroxide costs are estimated to be $70,000/yr. Also, 195 kg/day (430 lb) of sodium chloride and 53 kg/day (117 lb) of aluminum hydroxide are formed. The volume of neutralized solution is approximately 9461/ day (250 gal/day). Installed cost for a 379/1 (1000 gal) neutralizing, settling and hypochlorite decomposition system plus a small recirculating single-effect concentrator and crystallization system would be approximately $25,000. Operating costs including steam, electricity, disposal of solid wastes, labor and maintenance, and chemical costs would be approximately $12,000/yr. Overall costs of capital writeoff plus operating costs would be approximately $16,000/yr or slightly more than $2.20/kkg ($2/ton) of product.

Boiler Blowdowns, Cooling Tower Blowdowns, and Ion-Exchange Regenerants Treatment Systems and Their Costs

Present water treatment facilities in existing plants are usually not designed for zero discharge of water-borne wastes, nor are they designed for complete closed cycle operation. The generalized water treatment facilities given in Figure 63 earlier in this section provide three treatment techniques for removing dissolved solids from makeup and recycle water-demineralization, reverse osmosis and evaporation. It is assumed from the overall treatment model given in Figure 62 (of which Figure 63 is a detailed portion) that suspended solids and toxic materials have already been removed. Figure 83 gives the dissolved solids concentration range over which each type of treatment technique is economically feasible. Costs for different flow rates and dissolved solids contents are given in Table 77. This table shows that if all the incoming and recycle water and blowdowns are less than 1000 mg/l total dissolved solids then demineralizations can be used economically from 1000 mg/l to 3500 mg/l. Specialty demineralization systems are favorable, if available. Most blowdowns are in the 750 mg/l to 3500 mg/l range. Regenerants disposal adds to the overall demineralization costs. With these costs added, the specialty demineralization and reverse osmosis plus evaporation treatment costs are nearly equal in the 1000 mg/l to 3500 mg/l range. If any of the streams coming into the treatment area have greater than 3500 mg/l total dissolved solids, then reverse osmosis and/or evaporation are usually the only treatment approaches.

A model plant example is shown in Table 78 to illustrate needed equipment and costs for treatment.

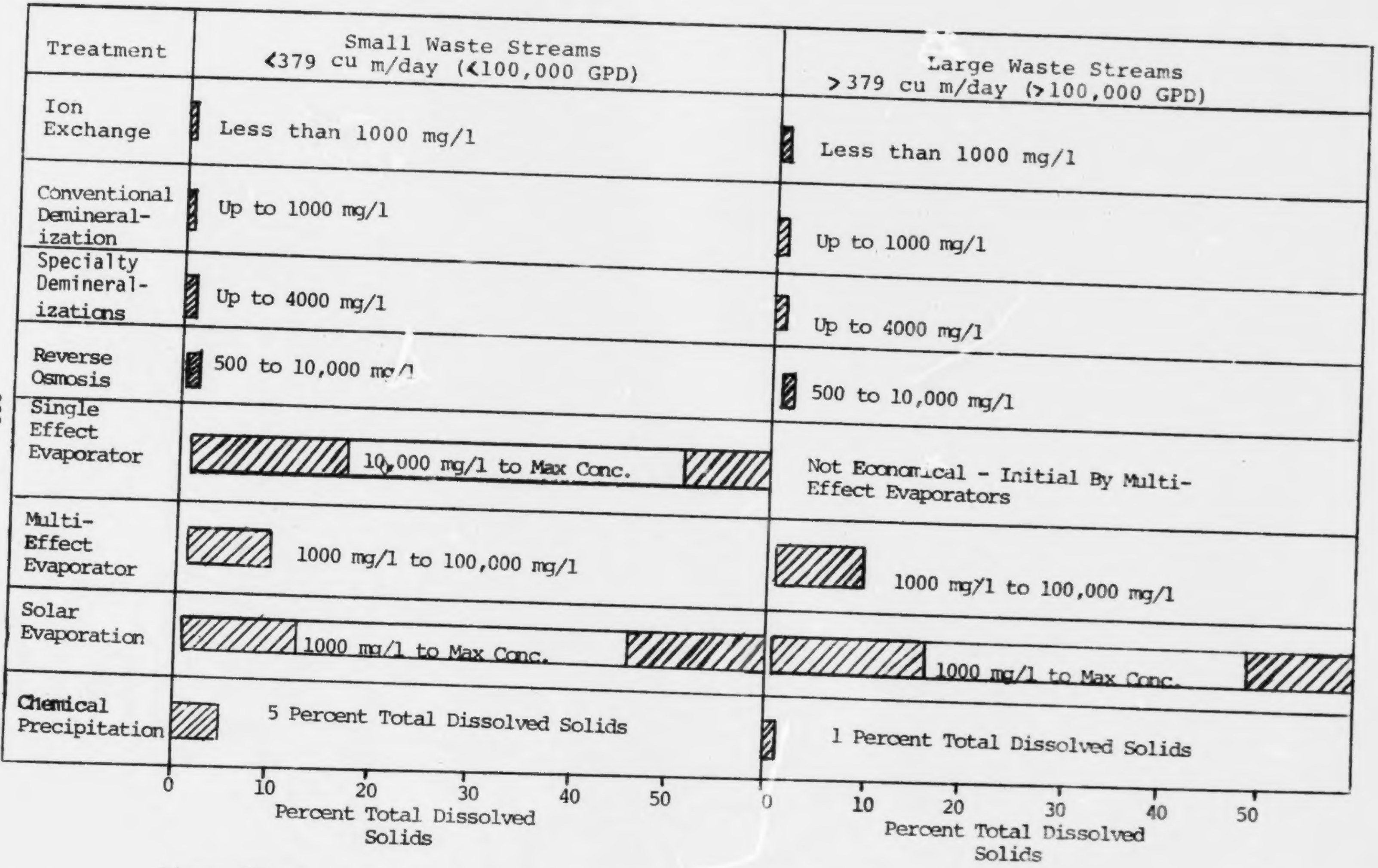


Figure 83. Treatment Applicability to Dissolved Solids Range in Waste Streams.

TABLE 77 Cost Estimates for Different Treatment

Flow cu m/d (GPD)	Demineralization Costs, $/day		Reverse Osmosis + Evaporation Costs, $/day
	100 mg/liter Total Dissolved Solids		
	Conventional Fixed-Bed		
38(10,000)	4		20
379(100,000)	31		142
3785(1,000,000)	220		1005
37850(10,000,000)	2000		6000
	1000 mg/liter Total Dissolved Solids		
	Conventional Fixed-Bed	Specialty Systems	
38(10,000)	13	7	20
379(100,000)	121	43	142
3785(1,000,000)	1120	335	1013
37850(10,000,000)	10,000	~3000	6275
	3500 mg/liter Total Dissolved Solids		
	Specialty Systems		
38(10,000)	12		20
379(100,000)	96		142
3785(1,000,000)	861		1013
37850(10,000,000)	8000		6275
	10,000 mg/liter Total Dissolved Solids		
38(10,000)	Costs are very high. This is above the application level.		20
379(100,000)			154
3785(1,000,000)			1115
37850(10,000,000)			7600

TABLE 78. Model Treatment Plant Calculations Design and Cost Basis

Waste Category	cu m/d (GPD)	Total Dissolved Solids, mg/l
Process Water	379(100,000)	10,000
Cooling Tower Blowdown	38(10,000)	1,000
Boiler Blowdowns	19(5,000)	500
Air Pollution Control	38(10,000)	10,000 (Recoverable at $33/kkg or $30/ton.)
Makeup Water	189(50,000)	300

Equipment Needed	cu m/d (GPD)	Capital Cost, $	
Demineralizer	379(100,000)	60,000	
Reverse Osmosis Unit	379(100,000)	80,000	
Multi-Effect Evaporator	94(25,000)	60,000	
2-Single-Effect Evaporators	38(10,000)	32,000	
Rotary DrumFilter	--	25,000	
Centrifuge	--	25,000	Total $282,000

Waste Treated	Overall Costs/Day
Process Water	$ 142
Cooling Tower Blowdown	$ 45
Boiler Blowdown	$ 45
Make-Up Water	$ 45
Air Pollution Control	($ 100 credit)
Net Cost	$ 85 or $30,000/yr.

In addition to the cost of treating the waste streams, approximately 36-45 kkg (40-50 ton) per day of solids must be disposed of. Disposal costs for these could range from $1.10 to $11.00 /kkg ($1 to $10/ton). A centralized treatment system as described gives not only zero water-borne waste but also supplies all the demineralized water needed for boilers, operation of cooling water towers at 95 to 98 percent recycle, and reduces process water wastes. Since the treatment equipment is all highly automated, labor costs are also low.

Geographic Influences on Treatment and Control Costs

Treatment and control practices and costs for the inorganic chemicals industry depend largely on plant location.

Ocean dumping may be economically feasible only for plants with easy access to the ocean. Even a difference of being located directly on ocean shores as contrasted to being 80 to 160 km (50 to 100 miles) up a bay or river can change barging costs by a factor of two. Ocean barging for titanium dioxide wastes may be as little as $5.50 /kkg ($5/ton) of product for well-suited plants. Costs may rise to $22-$44/kkg ($20 to $40 /ton) for others requiring more capital expenditures and longer barging distances.

Deep-well disposal may be geologically feasible in some parts of the United States but not in others. Brine well salt producers have traditionally deep-welled their wastes. Any other disposal method would raise the disposal costs significantly. An economically feasible method for disposal of wastes from the Solvay soda ash plants is deep-welling. However, deep-welling must be in accordance with local, State and Federal regulations.

Treatment and disposal situations and costs for eastern and western United States differ widely. Water is scarce in most of the west and, therefore, is worth more for recovery and reuse. Pure water may be worth 5.3¢ to 13.2¢/cu m (20¢ to 50¢/1000 gal).

Another difference between eastern and western U.S. is that the West generally has less rainfall. Except for some coastal and isolated areas, western United States has a positive evaporation-rainfall differential. This positive differential makes it possible to dispose of water-borne wastes by solar evaporation. Disposal costs as low as 7.9¢/cu m (30¢/1000 gal) were given earlier in this section. Comparable deep welling costs are 19.3¢/cu m (73¢/1000 gal).

The location, character, and size of the company-owned land around the plant is becoming increasingly important. Many of the older plants in the inorganic chemical industry are built on small plots, surrounded by industrial and residential neighbors. Industries such as hydrofluoric acid, titanium dioxide and sodium dichromate have heavy solid waste loads but often limited storage capacity. Even where wastes can be successfully disposed of outside the premises, costs are higher than for plant site storage.

SECTION IX

EFFLUENT REDUCTION ATTAINABLE THROUGH THE APPLICATION OF THE BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE

The effluent limitations which must be achieved by July 1, 1977 are based on the degree of effluent reduction attainable through the application of the best practicable control technology currently available. For the inorganic chemical industry, this level of technology was based on the best existing performance by exemplary plants of various sizes, ages and chemical processes within each of the industry's product subcategories.

Best practicable control technology currently available emphasizes treatment facilities at the end of a manufacturing process but also includes the control technology within the process itself when it is considered to be normal practice within an industry. Examples of waste management techniques which were considered normal practice within the inorganic chemicals industry are:

a. manufacturing process controls
b. recycle and alternative uses of water
c. recovery and/or reuse of waste water constituents.

Consideration was also given to:

a. The total cost of application of technology in relation to the effluent reduction benefits to be achieved from such application;
b. The size and age of equipment and facilities involved;
c. The process employed;
d. The engineering aspects of the application of various types of control techniques;
e. Process changes;
f. Non-water quality environmental impact (including energy requirements).

The following is a discussion of the best practicable treatment methods currently available for each of the chemical subcategories, and the effluent limitations on the significant pollutant parameters in their effluents.

EFFLUENT REDUCTION ATTAINABLE USING BEST PRACTICABLE TECHNOLOGY CURRENTLY AVAILABLE

Based upon the information contained in Sections III through VIII of this report, the following determinations were made on the degree of effluent reduction attainable by the application of the best practicable control technology currently available in the various subcategories of the inorganic chemicals industry.

General Water Guidelines

Process water is defined as any water directly contacting the reactants, intermediates, waste products, or end-products of a manufacturing process including contact cooling water. Not included in the guidelines are noncontact cooling water or ancillary waste streams resulting from steam and water supply. All values of guidelines and limitations presented below are expressed as kg of pollutant/kkg of product (lb/ton). While concentrations and flow are cited as the basis on which the guidelines were developed, the effluent limitations describe the allowable quantities of pollutants which may be discharged per unit of production. No limitations are established for either pollutant concentration or process waste water flow. The daily maximum limitation is double the thirty day average. Extensive, long-term data is not available for each of the 22 chemical subcategories. It was necessary, therefore, to rely on data from other segments of the inorganic chemicals industry, as well as data from other industrial categories. Based on this information and using good engineering judgement on the performance reliability of recommended treatment systems, a factor of two appears reasonable.

Aluminum Chloride

The process used for the manufacture of anhydrous aluminum chloride uses no water except in cases where a scrubber is employed to eliminate or reduce the discharge of unreacted chlorine gas. There are essentially three different grades of anhydrous aluminum chloride product made using the process of reacting chlorine gas with molten aluminum. The grey product is aluminum-rich, the white product is made from stoichiometric quantities of aluminum and chlorine, and the yellow product is chlorine-rich. The grey and white product manufacture releases little or no chlorine from the reactor and, therefore, dry collection methods can be employed to minimize air pollution. The manufacture of yellow product requires wet scrubbing to trap the excess chlorine gas.

An exemplary aluminum chloride plant uses a wet scrubber to produce a 28 percent aluminum chloride solution as a product for sale and has no water discharge. In cases where wet scrubbing is required and a favorable market for aluminum chloride solutions does not exist, the scrubber effluent may be treated to precipitate the aluminum salts from solution. The supernatant may then be recycled to the scrubber. Since the volume of water discharged from the scrubber system in plant 125 is only 2720 l/day (720 gal/day), another treatment approach consists of concentrating the scrubbing water with respect to aluminum chloride by recycling and then evaporating to dryness to recover additional product.

The effluent limitations guidelines for aluminum chloride plants based on best practicable technology currently available require no discharge of process waste water pollutants to navigable waters.

Aluminum Sulfate

Aluminum sulfate is made by digesting bauxite ore or aluminum clays in sulfuric acid. The wastes emanating from this process consist of insolubles such as iron and silicon oxides. These wastes are removed during settling and filtration of the product alum solution and also during washdown of tanks. In two exemplary plants (049 and 063), the waste muds are ponded to settle the solids and the clear water is recycled to the process. No process waste water pollutants are discharged. Costs for the entire aluminum sulfate industry to achieve this level of pollution control average $0.90/ton of product, which is approximately 1.5 percent of the list price of aluminum sulfate.

While it is recognized that the raw waste load generated by the manufacture of aluminum sulfate increases when aluminum clays or other impure raw materials are used as the source of aluminum, the production process is the same as for bauxite ore. Therefore, the use of raw materials other than bauxite ore does not preclude adoption of the best practicable technology currently available. One plant using clay as its raw material is able to totally recycle its process water.

Because of the negative water balance associated with aluminum sulfate production, the pond supernatant may be totally recycled with no discharge of process waste water pollutants. Muds and other impurities settle out and allow the supernatant to be reused without a build-up of contaminants. A discharge allowance is provided to permit the discharge of rainwater in excess of evaporation. This water must be treated to a 25 mg/l suspended solids concentration on the average and be within the pH range of 6.0 to 9.0. An untreated discharge is allowed in the event of a catastrophic rainfall in excess of the maximum 24-hour, 10-year rainfall event.

The effluent limitations guidelines for aluminum sulfate plants based on best practicable technology currently available require no discharge of process waste water pollutants to navigable waters.

No discharge of process waste water pollutants to navigable waters is also the effluent limitaion for plants producing iron-free alum. The production of iron-free alum requires pure raw metals, that is, iron-free sulfuric acid and iron-free hydrated alumina. The refining of the bauxite to produce the iron-free hydrated alumina yields wastes that must be segregated from the alum production process waters. The refining of bauxite to alumina is included in the nonferrous metal manufacturing point source category. Effluent guidelines for this refining process are presented therein.

Calcium Carbide

The data cited from plant 190 using an open furnace shows that the only manufacturing wastes involved are dusts emerging in tail gases from the furnaces. These are collected by dry bag filtration methods and are reused in the process or disposed of as solid wastes by landfilling. Dry bag collection of solid waste constitutes the best practicable control technology currently available. Because the segment of the calcium carbide industry covered herein is currently using this technology, no additional costs are required for treatment. Because plants manufacturing calcium carbide in covered furnaces typically recover the waste carbon monoxide, dry bag collection may be not universally applicable. Wet scrubbers are typically used to remove impurities from this gaseous stream. Hence, plants using covered furnaces are considered separately and wil be included in a forthcoming study.

The effluent limitations guidelines for calcium carbide plants using open furnace based on best practicable technology currently available require no discharge of process waste water pollutants to navigable waters.

Calcium Chloride

Calcium chloride is produced by extraction from natural brine and as a by-product of soda ash manufacture by the Solvay Process. The guidelines presented herein apply only to the brine extraction process.

The process wastes are weak brine solutions, which emanate from the blowdown of various brine purification steps and from several evaporation steps used in the process. The best practicable treatment technology is to pass the waste brine streams through ponds to settle suspended solids and adjust pH. Final ponding is used to remove additional suspended solids before discharge. The process water discharge flow averages 330 l/kkg of product (79 gal/ton), and contains suspended solids but no harmful metals.

The limitations are based on the performance of a well-designed and operated settling basin which will reduce the concentration of suspended solids to 25 mg/l. While it is recognized that significant quantities of dissolved solids may be present in the effluent, it was concluded that removal of these pollutants requires advanced treatment and expense beyond the definition of best practicable technology.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently available by calcium chloride plants using the brine extraction process:

TSS	0.0082 kg/kkg (0.0164 lb/ton)
pH	within the range 6.0 to 9.0

Calcium Oxide and Calcium Hydroxide

The manufacture of calcium oxide by the calcination of limestone is a dry process and uses only noncontact cooling water, and, in some cases, scrubber water. Plant 007 uses dry bag dust collectors and, therefore, discharges no process water. The use of dry bag collection methods is not contingent on the use of specific fuels for the calcination kilns nor is it geographically dependent. In plants with wet scrubbing systems already installed, the scrubbing solution may be reused in the process, or used to produce a low-grade product. One lime plant using wet scrubbers is able to completely recycle the scrubbing solution. Solids may be removed in settling vessels or ponds. For plants using ponds for treatment prior to reuse, a provision has been established to allow a discharge from impoundments in areas where rainfall exceeds evaporation. This discharge must be within the pH range of 6.0 to 9.0 and contain, on the average, a suspended solids concentration not to exceed 25 mg/l. In the event of a catastrophic rainfall exceeding the maximum 10-year, 24-hour event, an untreated discharge is allowed.

Plants using dry baghouses will not have to spend additional money to achieve the effluent reduction attainable by the application of best practicable technology currently available. Plants with wet scrubbers may have to invest up to an average of $1.28/ton of product.

The effluent limitations guidelines for calcium oxide and calcium hydroxide plants based on best practicable technology currently available require no discharge of process waste water pollutants to navigable waters.

Chlorine and Potassium or Sodium Hydroxide

(a) Diaphragm cell process

The diaphragm cell process for the manufacture of chlorine and caustic soda or caustic potash usually have the following raw wastes emanating from the process:

a. a solution of sodium hypochlorite and sodium bicarbonate from the scrubbing of chlorine tail gases (about 7.5 kg of dissolved solids/kkg of chlorine produced).
b. chlorinated organics from the liquifaction of chlorine gas (about 0.7 kg/kkg of chlorine produced)
c. brine wastes from the brine purification system (about 12.2 kg of dissolved solids /kkg of chlorine produced)
d. spent sulfuric acid from the chlorine drying process (about 4.2 kg/kkg of chlorine produced)
e. weak caustic and brine solution from the caustic evaporators using barometric condensers (about 9.5 kg of dissolved solids/kkg of chlorine produced)
f. weak caustic and brine solution from the caustic filter washdown (about 37.5/kg of dissolved solids/ kkg of chlorine produced).

At plant 157, the tail gas scrubber wastes are presently discharged. However, the installation of a chlorine burning hydrochloric acid plant will eliminate the scrubber wastes. This addition is practicable, as substantiated by plant 157's plans for installation in the near future. The chlorinated organics are disposed of by incineration. The brine wastes from brine purification are ponded to settle out suspended solids and the brine liquor is recycled to brine make-up. The spent sulfuric acid at this plant is utilized elsewhere in the complex or may be sent to a spent sulfuric acid plant for regeneration. Some plants presently use this acid to partially neutralize caustic wastes in the plant which aides in controlling the effluent pH. The weak caustic/brine solution from the caustic evaporators can be eliminated by replacing the barometric condensers with noncontact surface condensers or by recycling the discharge from the barometric condenser back to brine make-up. The weak caustic/brine solution from the caustic filters is presently pH adjusted and discharged. Diaphragm cell chlorine plants will need to invest approximately $0.30/ton of chlorine produced to implement best practicable technology currently available.

Lead is sometimes present in the effluent as a result of cracks around protective resin seals which encase underlying lead mountings. Currently one-third of the industry is using anodes which eliminate the lead discharge. Industry representatives state that another one-third are seriously considering conversion. The lead limitation is the average value discharged from three plants which have not converted to lead-free anodes. The suspended solids limitation is based on a well-operated sedimentation vessel or pond designed to treat suspended solids to a 25 mg/l concentration.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently available by diaphragm cell chlor-alkali plants:

TSS	0.32 kg/kkg (0.64 lb/ton)
Lead	0.0025 kg/kkg (0.005 lb/ton) of chlorine
pH	within the range 6.0 to 9.0

(b) Mercury cell process

The mercury cell process for the manufacture of chlorine and caustic soda or caustic potash usually has similar wastes to the diaphragm cell process. The major exception is the loss of mercury from the process. Exemplary plants 144, 098 and 130 have excellent mercury control systems to minimize the incorporation of mercury into discharge streams. These controls consist of curbing the cell area to retain mercury lost in spills or leaks, collecting all mercury before ponding and discharge and/or recycling mercury-containing waste water back to the cells for reuse after treatment to remove any impurities. These plants have continuous mercury monitors on streams possibly contaminated that are meant for ponding to settle suspended solids before discharge. The mercury recommendation is twice the discharge performance achieved by the three plants studied, whose discharges per ton of chlorine are very similar. The mercury limitation represents the quantity of mercury discharged from the mercury treatment system. Residual mercury may be present in other portions of the plant and may contribute to the total mercury discharge. Residual mercury levels are difficult to quantify on a production basis and are, therefore, not the subject of the limitations presented below. Costs for the industry to achieve best practicable technology currently available are estimated to be $2.74/ton of chlorine produced.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently available by mercury cell chlor-alkali plants:

TSS	0.32 kg/kkg (0.65 lb/ton) of chlorine
Mercury	0.00014 kg/kkg (0.00028 lb/ton) of chlorine
pH	within the range 6.0 to 9.0

Hydrochloric Acid

The manufacture of hydrochloric acid by the chlorine burning process comprises a minor part of total U.S. production. All of the chlorine burning facilities are located within chlor-alkali complexes. Plant 121 is one such facility. The only waste generated from this process consists of weak hydrochloric acid, which is generated only during startup of the operation. No waste emanates from the process during normal operation. The startup weak acid waste is normally neutralized with sodium hydroxide which yields dissolved solids (sodium chloride) amounting to about 0.5 kg/kkg (1 lb/ton) of product acid. The weak brine startup waste from the hydrochloric acid plant may be utilized in the brine make-up operation at the chlor-alkali portion of the complex, reused in acid manufacture.

Any leaks and spills must be contained and collected. If adequately segregated from other waste streams, the spills and leaks may be reused or sold. Good housekeeping, operation and maintenance will minimize or eliminate leaks and spills.

The effluent limitations guidelines for chlorine-burning hydrochloric acid plants based on best practicable technology currently available require no discharge of process waste water pollutants to navigable waters.

Hydrofluoric Acid

The manufacture of hydrofluoric acid by the reaction of fluospar (about 97 percent calcium fluoride) with sulfuric acid generates about 3.1-3.6 kkg (3.5 - 4.0 tons) of solid waste/kkg of product acid. All wastes from the process may be water slurried to settling ponds, and the clear liquid recycled. All process water can be segregated from noncontact cooling water. At least one plant in the industry uses this recycle technology to eliminate its process waste water discharge.

All leaks and spills must be contained and may be recycled, sold or pumped to the settling pond for treatment prior to reuse. Good housekeeping, operation, and maintenance will minimize or eliminate leaks and spills. A discharge is permitted from the impoundment if rainfall exceeds evaporation, or in the event of a catastrophic rainfall in excess of the maximum 24-hour, 10-year event. Except from discharges as a result of a catastrophic rainfall, the thirty-day average concentration of any effluent must not exceed 25 mg/l suspended solids and 15 mg/l fluoride. The pH must be within the range 6.0 to 9.0.

The effluent limitations guidelines for hydrofluoric acid plants based on best practicable technology currently available require no discharge of process waste water pollutants to navigable waters.

Hydrogen Peroxide

(a) Organic process

The organic process for the manufacture of hydrogen peroxide at plant 069 generates a waste stream containing 0.17-0.35 kg/kkg (0.34-0.70 lb/ton) of organics. The treatment methods currently used at this plant include an 80 percent reduction of hydrogen peroxide to water and oxygen, a recovery system which recovers 60-70 percent of lost organics, and tank diking and process curbing to retain waste spills. The process water use in this facility is 16,000 l/kkg of product (3,800 gal/ton) and contains, after treatment, suspended solids and organic matter, but no harmful metals. The guidelines are based on the treatment systems used at plant 069 and the actual performance of these operations. The cost to implement these technologies is estimated to be $1.00/ton of product.

The following limitations constitute the quanitity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently available by organic process hydrogen peroxide plants:

TSS	0.40 kg/kkg (0.80 lb/ton)
TOC	0.22 kg/kkg (0.44 lb/ton)
pH	within the range 6.0 to 9.0

(b) Electrolytic process

There is only one plant in the U.S. that makes hydrogen peroxide by the electrolytic process. Plant 100 recovers all of the solids present in the process wastes and uses an ion exchange system to remove 98 percent of the cyanides present in the waste stream before discharge. The ion exchange regenerant is pH controlled prior to discharge. The effluent limitations are based on the performance of treatment systems employed at plant 100. Suspended solids are discharged in concentrations less than 25 mg/l and the oxidizable cyanide concentration averages 2 mg/l.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently available by electrolytic process hydrogen peroxide plants:

TSS	0.0025 kg/kkg (0.005 lb/ton)
Cyanide	0.0002 kg/kkg (0.0004 lb/ton)
pH	within the range 6.0 to 9.0

Nitric Acid

Commercial grade nitric acid (up to 70 percent concentration) is made by the oxidation of ammonia. At plant 114, all process waters are recycled with no discharge of process waste water pollutants. Of the 30,280 cu m (8 million gal) of water/day used for cooling, about 95 percent is recycled. An additional 757 cu m/day (0.02 mgd) are used to make steam and 75 percent of this quantity is recycled. About 87 cu m (23,000 gal)/day of steam condensate is used for acid make-up water. The discharge from the plant consists of noncontact cooling water which contains blowdowns from boilers, cooling towers and water treatment with a total waste load amounting to about 2 kg/kkg (4 lb/ton) of product produced.

The best practicable treatment technology available for commercial grade nitric acid plants is the recycle of all process waters and the segregation of process waters from cooling water as demonstrated in plant 114. Volumes of waste water as a result of leaks and spills may be minimized or eliminated by good housekeeping, operation and equipment maintenance. These waste waters should be collected and may be recycled with the weak acid streams from condensers or may be sold as a weak acid product. It is estimated that $0.22/ton of product is required to implement these technologies.

The effluent limitations guidelines for plants producing nitric acid up to 70 percent concentration based on best practicable technology currently available require no discharge of process waste water pollutants to navigable waters.

Potassium Metal

Plant 045 produces most of the potassium metal manufactured in the U.S. by a completely dry process. No water is used. Therefore, the effluent limitations guidelines based on best practicable technology currently available require no discharge of process waste water pollutants to navigable waters.

Potassium Dichromate

The process for the production of potassium dichromate involves the reaction of potassium chloride with sodium dichromate. At plant 002, all process water is recycled and sodium chloride (400 kg/kkg of product) is removed as a solid waste. The only water-borne waste source is contamination of cooling water by hexavalent chromium in a barometric condenser presently in use on the product crystallizer. The plant has plans to replace the barometric condenser with a noncontact heat exchanger which will eliminate cooling water contamination. Best practicable technology currently available requires total recycle of process waste waters. The waste liquor from the salt concentrator may be recycled to the reaction mix tank. Chromium discharges may be eliminated by installing noncontact heat exchangers. Costs to implement these technologies are estimated to be $4.65/ton of product. This is approximately one percent of the list price of potassium dichromate.

The effluent limitations guidelines for potassium dichromate plants based on best practicable technology currently available require no discharge of process waste water pollutants to navigable waters.

Potassium Sulfate

All of the potassium sulfate manufacturers in the U.S. are located in the arid southwest near deposits of langbeinite ore ($K_2SO_4 . 2MgSO_4$). The reaction of this ore with a potassium chloride solution and the subsequent crystallization and separation of potassium sulfate from magnesium chloride brine constitutes the process for the production of potassium sulfate. A large amount (about 2000 kg/kkg of product) of magnesium chloride brine is a co-product of this process. Plant 118 sells most of this brine when the sodium content of the ore is low. It ponds the brine for evaporation when it cannot be sold. Evaporation ponds in this area of the country are feasible. The cost of water is a problem and most of the liquor in the brine is recycled back to the process for reuse before the magnesium chloride is sold or dumped. Other insoluble wastes from the process muds amount to about 15 kg/kkg of product, and they are landfilled. Because of the geographical dependence of plants manufacturing potassium sulfate to the arid southwest evaporation ponds are considered to be the best practicable technology currently available.

The effluent limitations guidelines for potassium sulfate plants based on best practicable technology currently available require no discharge of process waste water pollutants to navigable waters.

Sodium Bicarbonate

Sodium bicarbonate is manufactured by the carbonation of a sodium carbonate solution. Most plants are located in or near complexes manufacturing soda ash by the Solvay Process. There is one isolated facility which uses mined soda ash as a raw material. Plant 166 is located within a Solvay Process complex. The major wastes from this process are about 10 kg of undissolved sodium bicarbonate/kkg of product and an average of about 38 kg of dissolved sodium bicarbonate/kkg of product. Some of the undissolved sodium bicarbonate is reusable and it is redissolved and recycled to the process. The remainder is landfilled along with sand from the filters and other non-process solid waste. The weak slurry thickener overflow, which constitutes their present source of waste, may be used as a source of liquid for the product dryer scrubber. Recycling this liquid to concentrate it with respect to sodium carbonate will enable it to be reused in the process. These process changes will eliminate the discharge of process waste waters. One plant plans to incorporate this technology into its manufacturing process.

Costs for implementation of best practicable technology currently available are expected to be offset by recovered product values.

The effluent limitations guidelines for sodium bicarbonate plants based on best practicable technology currently available require no discharge of process waste water pollutants to navigable waters.

Sodium Carbonate

The Solvay Process for the manufacture of sodium carbonate (soda ash) involves the reaction of sodium chloride brine, ammonia and carbon dioxide to yield crude soda ash. The ammonia is recovered from the process by reacting the spent brine solution with lime followed by distillation. This process produces about 1500 kg of dissolved solids waste/kkg of soda ash manufactured. Calcium chloride comprises the majority of this waste, amounting to about 1050 kg for every kkg of soda ash. Plant 166 recovers about 21 percent of the waste calcium chloride for sale. The total recovery of calcium chloride is not practical because of the limited market. The only treatment used at this plant is a settling pond to reduce the concentration of suspended solids in the effluent. Therefore the effluent limitations guidelines are not based on by-product recovery, but upon the water flow necessary to maintain the total calcium chloride by-product formed in the process at a 10 percent concentration at discharge 900 l/kkg of soda ash (1,650 gal/ton). Suspended solids but no harmful metals may also be present. Large quantities of dissolved solids, primarily chlorides, are generally present in the effluent. Considering the available treatment technologies to remove chlorides and their associated costs, it was concluded that, in this case, dissolved solids removal is beyond the scope of best practicable technology currently available.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently available by sodium carbonate plants using the Solvay Process:

TSS	0.17 kg/kkg (0.34 lb/ton)
pH	within the range 6.0 to 9.0

Sodium Metal

The process for the manufacture of sodium metal, commonly called the Downs Cell Process, is essentially dry. However, water-borne wastes are generated during cleanout and washdown of cells when the electrolyte is replenished, from scrubbing chlorine tail gases and from drying the chlorine with sulfuric acid. At plant 096, the spent drying acid is not discharged but used elsewhere in the works complex. The wastes from cell wash-downs, runoff water and residual chlorine-containing water from the tail gas scrubber are ponded to settle suspended solids and then discharged. At plants where the utilization of the spent drying acid and calcium hypochlorite solution is not possible, the spent acid may be recovered or sold to a "decomp" sulfuric acid plant and the calcium hypochlorite solution be recovered and marketed as a bleach product. The limitations are based on the discharge volume of process water other than barometric condensers which contributes only small quantities of TSS. Treatment of the process water in well-designed settling basins to a 25 mg/l concentration is considered to be best practicable technology currently available.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently available by sodium metal manufacture plants:

TSS	0.23 kg/kkg (0.46 lb/ton)
pH	within the range 6.0 to 9.0

Sodium Chloride

(a) Solar evaporation process

Solar salt is produced by the long-term solar evaporation of sea water to precipitate sodium chloride. This process generates a bittern waste solution consisting mainly of sodium, potassium and magnesium salts. Plant 059 reclaims some of the waste salts from the bitterns and stores the rest for future reclamation. Because this impoundment procedure is dependent on the availability of large areas of land for storage ponds, it may not be generally applicable. Until recovery of magnesium and potassium values proves economical, unused bitterns may be returned to the source of the original brine solution provided that no additional pollutants are added.

(b) Solution brine-mining process

Sodium chloride manufacture by this process involves pumping water into an underground salt deposit (solution mining) and returning the brine for treatment to remove impurities. Multiple effect evaporators are used to crystallize and collect the pure sodium chloride for sale. At plant 030, the brine sludges from the brine purification step are disposed of by returning them to the mine. Other sources of waste water are the purges from the evaporators, spills and the barometric condenser. All of the concentrated brine wastes are recycled to the process. The current plant effluent is neutral in pH and low in suspended solids. Best practicable technology currently available consists of treating the solid-containing waste streams in a well-designed and operated settling pond.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently available by solution mining evaporative process sodium chloride plants:

TSS	0.15 kg/kkg (0.30 lb/ton)
pH	within the range 6.0 to 9.0

Sodium Dichromate and Sodium Sulfate

These two chemicals are manufactured as co-products by the calcination of a mixture of chrome ore, soda ash and lime followed by water leaching and acidification of the soluble chromates. The sodium sulfate product is crystallized out after acidification. The bulk of the waste originates from the undigested portions of the ore and is mostly solid wastes. Water-borne wastes arising from spills and washdowns contain most of the hexavalent chromium. Treatment at plant 184 consists of containment of spills, leaks and rain water runoff in chromate areas of the plant, followed by treating the chromium-containing waste water with pickle liquor to affect reduction of the chromates and then lagooning to settle suspended solids before discharge. This treatment removes 99 percent of the hexavalent chromium. Dichromate plant 014 uses the more conventional sodium hydrosulfide treatment to reduce the hexavalent chromium. Subsequent lime treatment limits the discharge to the solubility limits of calcium sulfate (2000 mg/l) and about 0.05 mg/l of unreacted hexavalent chromium and a total chromium level of 0.44 mg/l. The effluent limitations are based on chromium treatment to these levels and suspended solids removal in a well-operated settling basin, designed to reduce TSS to a 25 mg/l concentration. Costs to achieve this treatment level are estimated to be $16/ton of sodium dichromate which is about 4.6 percent of its list price.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently available by sodium dichromate and sodium sulfate coproduct plants:

TSS	0.22 kg/kkg (0.44 lb/ton)
Cr(+6)	0.0009 kg/kkg (0.0018 lb/ton)
Cr(T)	0.0044 kg/kkg (0.0088 lb/ton)
pH	within the range 6.0 to 9.0

Sodium Silicate

Sodium silicate is produced by the reaction of soda ash and silica in a furnace to form a sodium silicate glass. The material is sold either as a solid glass product or is pressure dissolved in water and sold as a solution with various ratios of silica to sodium oxide. The water-borne waste generated consists of unreacted silica, sodium hydroxide and sodium silicate from tank washdowns, product shock cooling with water and scrubber effluent. At plant 072, these wastes are ponded to settle the solids and the clear liquid is partially recycled. Best practicable technology currently available consists of sedimentation and neutralization of the effluent. The suspended solids settle efficiently and the waste water should contain only dissolved sodium sulfate and virtually no sodium silicate.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable technology currently available by sodium silicate plants:

TSS	0.005 kg/kkg (0.01 lb/ton)
pH	within the range 6.0 to 9.0

Sodium Sulfite

Sodium sulfite is manufactured by the reaction of sulfur dioxide with soda ash. The process wastes are mainly sulfides from product purification and sodium sulfite/sodium sulfate solutions from the product dryer ejector, filter washings and vessel cleanouts. Plant 168 is the only sodium sulfite plant currently treating the waste sulfite-containing solutions to oxidize sulfite to sulfate. The efficiency of this aeration treatment is about 94 percent. This treatment reduces the COD to the level required by best practicable technology currently available. An additional filtration treatment is given to the process waste water which removes 98 percent of the suspended solids. This treatment reduces TSS to below 25 mg/l. The limitations are based on the waste stream emanating from the dryer ejector and filter wash operations of this plant at the high end of its range (630 l/kkg or 150 gal/ton).

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently available by sodium sulfite plants:

TSS	0.016 kg/kkg (0.032 lb/ton)
COD	1.7 kg of dichromate ion/kkg
pH	within the range 6.0 to 9.0

Sulfuric Acid

Sulfuric acid is manufactured using the sulfur-burning contact process by three different types of plants. These are single absorption plants, double absorption plants and spent acid plants. The guidelines presented herein do not apply to spent acid plants or by-product sulfuric acid production, as in copper smelting operations.

Plant 141 is a single absorption plant and plant 086 is a double absorption plant. The double absorption plant has no process waste and uses only noncontact cooling water. The single absorption plant requires the use of wet scrubbing to minimize air pollution, and the scrubber water is recycled. There is no discharge of process waste water from these plants. A sulfuric acid plant in Finland neutralizes its scrubber water. The salt solution is then concentrated into fertilizer feed. Leaks and spills may be minimized or eliminated by good housekeeping, operation and equipment maintenance. Leaks should be segregated from other waste streams and may be reused in the process or sold as a weak acid solution.

The effluent limitations guidelines for single and double absorption sulfur burning sulfuric acid plants based on best practicable technology currently available require no discharge of process waste water pollutants to navigable waters.

Titanium Dioxide

a) Chloride process

Chloride process plant 039 uses neutralization, clarification and ponding to settle suspended solids and to precipitate metals. About 93 percent of the cooling water is recycled but there appears to be no practical approach for recycling process water. Deep well disposal is utilized by another company (plant 160). The plant effluent is neutral pH and contains mostly sodium chloride as the dissolved solid.

Best practicable technology currently available consists of lime treatment and sedimentation to reduce the iron concentration to 4 mg/l and the TSS to 25 mg/l. The guidelines are only applicable to discharges resulting from titanium dioxide production. They do not include any wastes resulting from ore beneficiation. In some cases, all titanium tetrachloride is not used to produce titanium dioxide. The guidelines include only those wastes which may be attributed to titanium dioxide production.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently available by titanium dioxide plants using the chloride process:

TSS	2.2 kg/kkg (4.4 lbs/ton)
Iron	0.36 kg/kkg (0.72 lb/ton)
pH	within the range 6.0 to 9.0

b) Sulfate process

The high iron content in the ilmenite ore raw material is a major source of the wastes generated by this process. Another major contributor to the process waste is the large amount of spent sulfuric acid from digestion of the ore. Very little treatment is presently being used and The effluents from these plants are highly acidic and contain high concentrations of suspended and dissolved solids including metal ions. Ocean barging is used by some to dispose of the process waste waters. Plant 122 is presently installing treatment facilities to neutralize and oxidize the process waste to remove acid as calcium sulfate, to reduce the chemical oxygen demand and reduce the concentration of harmful metal ions. Additional settling ponds are planned to reduce the quantities of suspended solids formed during the neutralization treatment. Considerable research is being done to improve treatment technologies for this process. Best practicable technology currently available consists of lime neutralization and settling. This treatment system will remove iron and suspended solids, while coprecipitating other metal ions such as vanadium, chromium, and manganese. The limitations are based on a suspended solids concentration of 50 mg/l and an iron concentration of 4 mg/l. A flow basis of 210,000 l/kkg was used. This flow may be achieved by recycling scrubber water to the process.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently available by sulfate process titanium dioxide plants:

TSS	10.5 kg/kkg (21.0 lb/ton)
Iron	0.84 kg/kkg (1.68 lb/ton)
pH	within the range 6.0 to 9.0

SECTION X

EFFLUENT REDUCTION ATTAINABLE THROUGH THE APPLICATION OF THE BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE,

The effluent limitations which must be achieved by July 1, 1983 are based on the degree of effluent reduction attainable through the application of the best available technology economically achievable. For the inorganic chemical industry, this level of technology was based on the best control and treatment technology employed by a point source within the product subcategory, or where it is readily transferable from one industry process to another.

The following factors were taken into consideration in determining the best available technology economically achievable:

a. the age of equipment and facilities involved;
b. the process employed;
c. the engineering aspects of the application of various types of control techniques;
d. process changes;
e. cost of achieving the effluent reduction resulting from application of the best available technology economically achievable; and
f. non-water quality environmental impact (including energy requirements).

In contrast to the best practicable technology currently available, best available technology economically achievable assesses the availability in all cases of in-process controls as well as control or additional treatment techniques employed at the end of a production process. In-process control options available which were considered in establishing these control and treatment technologies include the following:

a. alternative water uses
b. water conservation
c. waste stream segregation
d. water reuse
e. cascading water uses
f. by-product recovery
g. reuse of waste water constituent
h. waste treatment
i. good housekeeping
j. preventive maintenance
k. quality control (raw material, product, effluent)
l. monitoring and alarm systems.

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Those plant processes and control technologies which at the pilot plant, semi-works, or other level, have demonstrated both technological performances and economic viability at a level sufficient to reasonably justify investing in such facilities were also considered in assessing the best available technology economically achievable. It is the highest degree of control technology that has been achieved and has been demonstrated to be capable of being designed for plant scale operation. Although economic factors are considered in this development, the costs for this level of control are intended to be for the top-of-the line of current technology subject to limitations imposed by economic and engineering feasibility. However, this technology may necessitate some industrially sponsored development work prior to its application.

EFFLUENT REDUCTION ATTAINABLE USING BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE

Based upon the information contained in Sections III through IX of this report, the following determinations were made on the degree of effluent reduction attainable by the application of the best available control technology economically achievable in the various categories of the inorganic chemical industry.

General Water Guidelines

Process water is defined as any water contacting the reactants of a process including contact cooling water. All values of guidelines and limitations presented below are expressed as thirty-day averages in units of kg of parameter per metric ton (lbs/ton) of product produced. The daily maximum limitation is double the monthly average, as discussed in section IX. For those subcategories which utilize impoundments to achieve no discharge of process waste water pollutants, an untreated discharge is allowed in the event of a catastrophic rainfall exceeding the maximum 25 year, 24 hour rainfall event.

No discharge of process waste water pollutants to navigable waters is attainable by the application of the best practicable technology currently available for the following chemical subcategories:

aluminum chloride
aluminum sulfate
calcium carbide
calcium oxide and calcium hydroxide
hydrochloric acid
hydrofluoric acid
nitric acid
potassium metal
potassium dichromate
potassium sulfate
sodium bicarbonate
sulfuric acid

The same effluent reduction is required for these subcategories based on best available technology economically ahcievable.

Calcium Chloride

Best available technology economically achievable includes recycle of the packaging area washdown water and use of noncontact heat exchangers. These process changes are being planned by plant 185.

Therefore, the effluent limitations guidelines for calcium chloride based on the application of the best available technology economically achievable require no discharge of process waste water pollutants to navigable waters.

Hydrogen Peroxide

a) Organic process

Best available technology for organic process hydrogen peroxide plants is to recycle all process water. The discharged process water presently contains hydrogen peroxide and organic solvent which should not be detrimental to the process. Carbon adsorption techniques may be applied if necessary prior to water reuse. The effectiveness of this treatment for organic removal has been widely demonstrated.

The effluent limitations guidelines for hydrogen peroxide production by the organic process based on the application of the best available technology economically achievable require no discharge of process waste water pollutants to navigable waters.

b) Electrolytic process

Best available technology for this process is segregation of the process waste water from the cooling water discharge, treatment of the relatively small amount of process waste water by distillation. The distillate may be reused in the process. This is feasible because the process waste water flow is only 95 l/kkg (25 gal/ton) in the one plant using this process.

The effluent limitations guidelines for electrolytic process hydrogen peroxide plants based on the application of the best available technology economically achievable require no discharge of process waste water pollutants to navigable waters.

Sodium Carbonate

The calcium chloride raw waste load of the Solvay process is such that 10-15 percent of it can supply the total volume of the current U.S. market for calcium chloride, so the potential for waste disposal through this channel may be limited. Large capital costs are involved to bring Solvay process plants to the capability of zero discharge, and the disposal of the by-product calcium chloride is difficult due to its extreme solubility. However, technology does exist to further reduce the concentration of suspended solids in the effluent to 15 mg/l or to reduce the volume of process water required.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after the application of best available technology economically achievable for soda ash produced by the Solvay process:

TSS	0.10 kg/kkg (0.20 lb/ton)
pH	within the range 6.0 to 9.0

Sodium Chloride

a) Solar evaporation process

Consistent with the effluent reduction attainable by the application of best practicable technology, unused bitterns may be returned to the brine source provided no additional pollutants are added.

b) Solution brine-mining process

The major source of the discharged sodium chloride dissolved solids waste generated at plant 030 emanates from carryover in the barometric condensers. The best available technology economically achievable for brine mining evaporative process sodium chloride plants is to replace the barometric condensers with noncontact heat exchangers and recycle the steam condensate to the evaporators. The effluent limitations guidelines for evaporative process sodium chloride plants based on the application of the best available technology economically achievable require no discharge of process waste water pollutants to navigable waters.

Sodium Metal

Best available technology for sodium metal plants is:

a. Recycle of the wastes from cell washdowns to brine purification after removal of suspended solids.
b. Recovery of the calcium hypochlorite waste from the tail gas scrubber as a product and recycle of water to the scrubber. or replace the scrubber with a chlorine-burning hydrochloric acid facility.

c. Recycle the spent sulfuric acid used for drying the chlorine to a "decomp" sulfuric acid plant or sale as a weak acid solution.

Implementation of these technologies will eliminate the discharge of process waste water pollutants.

The effluent limitations guidelines for sodium metal-chlorine plants based on the application of the best available technology economically achievable require no discharge of process waste water pollutants to navigable waters.

Sodium Sulfite

Best available technology for sodium sulfite plants is recovery of the sodium sulfate from the waste discharge by evaporation and sale as a by-product or satisfactory land disposal. This should not be too costly since the volume of effluent from plant 168, for example, averages only 1426.5 cu m/day (3700-7000 gal/day), and the dissolved solids in this stream are mostly sodium sulfate.

The effluent limitations guidelines for sodium sulfite plants based on the application of the best available technology economically achievable require no discharge of process waste water pollutants to navigable waters.

Chlorine and Sodium or Potassium Hydroxide

a) Diaphragm cell process

Best practicable technology currently available for the manufacture of chlorine and caustic soda or caustic potash by the diaphragm cell process allows the discharge of treated wastes from the tail gas scrubber and of neutralized spent acid from chlorine drying. Best available technology is elimination of the pollutant discharge by:

a. Catalytic treatment of the hypochlorite waste from the scrubber to convert to a brine and recycle to brine purification, recovery of the hypochlorite as a bleach product or elimination of the scrubber and utilization of the chlorine gas elsewhere in the plant, such as in a chlorine-burning hydrochloric acid plant;
b. Recovery of the spent acid from chlorine drying and sale, utilization elsewhere in the plant or return to spent sulfuric acid plant for regeneration; and
c. Recycle of all weak brine/caustic solutions to the process after extraction/elimination of harmful metals and impurities.

The effluent limitations guidelines for diaphragm cell chlor-alkali plants based on the application of the best available technology economically achievable require no discharge of process waste water pollutants to navigable waters.

b) Mercury cell process

The same technologies cited above for diaphragm cell plants apply to mercury cell plants.

The effluent limitations guidelines for mercury cell chlor-alkali plants based on the application of the best available technology economically achievable require no discharge of process waste water pollutants to navigable waters.

Sodium Dichromate and Sodium Sulfate

At plant 184, a total of approximately 113,000 kkg of product and by-product are manufactured annually. The additional treatment cost to this plant for the evaporation of the effluent to effect zero discharge would amount to about $250,000/yr. This would mean an approximate cost of $2.20/kkg of sodium dichromate and sodium sulfate.

The effluent limiations guidelines for sodium dichromate and byproduct sodium sulfate plants, based on the application of the best available technology economically achievable require no discharge of process waste water pollutants to navigable waters.

Titanium Dioxide

As indicated in Section VIII of this report, the additional treatment costs projected to bring each of these processes (chloride and sulfate) to zero discharge of process waste water pollutants by demineralization and evaporation of regenerant solutions are as follows:

a. Chloride process - an additional $730,000 per year for a plant with a 24,300 kkg (27,000 ton) per year capacity or an increase of approximately 5 percent over the costs of best practicable technology.
b. Sulfate process - an additional $620,000 per year for a plant with a 39,600 kkg (43,000 ton) per year capacity or an increase of approximately 3 percent over the costs of best practicable technology

However, evaporation of the large amounts of water necessary in both processes would consume large amounts of energy and solid waste disposal costs are high. The technology does exist to further reduce the concentration of suspended solids and iron.

Best available technology economically achievable consists of water conservation and more efficient suspended solids removal than required by the 1977 standard. The following limitations constitute the quantity of pollutants which may be discharged after application of the best available technology economically achievable by titanium dioxide plants:

a. Chloride Process:

TSS	1.3 kg/kkg (2.6 lbs/ton)
Iron	0.18 kg/kkg (0.36 lb/ton)
pH	within the range 6.0 to 9.0

b. Sulfate Process:

TSS	5.3 kg/kkg (10.6 lbs/ton)
Iron	0.42 kg/kkg (0.84 lb/ton)
pH	within the range 6.0 to 9.0

SECTION XI

NEW SOURCES PERFORMANCE STANDARDS AND PRETREATMENT STANDARDS,

The term "new source" is defined in the Act to mean "any source, the construction of which is commenced after the publication of proposed regulations prescribing a standard of performance". The treatment technology for new sources is evaluated by adding to the considerations underlying the identification of best available technology economically achievable, a determination of what higher levels of pollution control are available through the use of improved production processes and/or treatment techniques. Thus, in addition to considering the best in-plant and end-of-process control technology, new source performance standards reflect how the level of effluent may be reduced by changing the production process itself. Alternative processes, operating methods or other alternatives were considered. However, the end result of the analysis identifies effluent standards which reflect levels of control achievable through the use of improved production processes (as well as control technology), rather than prescribing a particular type of process or technology which must be employed.

The following factors were considered in assessing the best demonstrated control technology currently available for new sources:

(a) the type of process employed and process changes;
(b) operating methods;
(c) batch as opposed to continuous operations;
(d) use of alternative raw materials and mixes of raw materials;
(e) use of dry rather than wet processes (including substitution of recoverable solvents for water); and
(f) recovery of pollutants as by-products.

In addition to the effluent limitations covering discharges directly into waterways, the constituents of the effluent discharge from a plant within the industrial category which would interfere with, pass through, or otherwise be incompatible with a well-designed and operated publicly owned activated sludge or trickling filter waste water treatment plant were identified.

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EFFLUENT REDUCTION ATTAINABLE BY THE APPLICATION OF THE BEST AVAILABLE DEMONSTRATED CONTROL TECHNOLOGIES, PROCESSES, OPERATING METHODS OR OTHER ALTERNATIVES.

Based upon the information contained in Sections III through X of this report, the following determinations were made on the degree of effluent reduction attainable with the application of new source standards for the various subcategories of the inorganic chemicals industry.

No discharge of process waste water pollutants to navigable waters is the new source performance standard for the following chemical subcategories:

- aluminum chloride
- aluminum sulfate
- calcium carbide
- hydrochloric acid
- hydrofluoric acid
- calcium oxide and calcium hydroxide
- nitric acid
- potassium metal
- potassium dichromate
- potassium sulfate
- sodium bicarbonate
- sulfuric acid

This is achievable by the application of the best practicable technology currently available.

The new source performance standards for the following chemicals require no discharge of process waste water pollutants to navigable waters:

- calcium chloride
- hydrogen peroxide
- sodium metal
- sodium chloride
    - a) solution brine-mining process

This standard may be achieved by the incorporation of best available technologies economically achievable into new sources. The technologies, as outlined in Section X, have been demonstrated and may be included in the design of new sources.

Chlorine

New source performance standards for chlorine are based on the application of best practicable technology currently available, as summarized in Section IX. Metal anodes may be used to eliminate the discharge of lead, as required for new plants.

Sodium Carbonate

An alternative process for the manufacture of soda ash with no discharge of process waste water pollutants exists, the mining and processing of trona. Because of this, no discharge of process waste water pollutants to navigable waters is the new source performance standard for this manufacturing process. The calcium chloride raw waste load of the Solvay process is such that 10 to 15 percent of it can supply the total volume of the U.S. market. Large capital costs are involved to bring Solvay process plants to the capability of no discharge, and the disposal of the unmarketable by-product calcium chloride is difficult due to its extreme solubility. No new Solvay process plants have been built in forty years. The supply of trona ore is adequate to satisfy the demand for sodium carbonate.

Sodium Chloride

The new source performance standards represent the effluent reduction attainable by the application of the best practicable technology currently available as described in Section IX.

Sodium Dichromate and Sodium Sulfate

The new source performance standards for sodium dichromate and by product sodium sulfate plants represent the application of best practicable technology currently available and require good water conservation which is possible in the construction of new facilities.

The new source performance standards for this subcategory are:

TSS	0.15 kg/kkg (0.3 lb/ton)
Cr(T)	0.0044 kg/kkg (0.0088 lb/ton)
Cr(+6)	0.0005 kg/kkg (0.001 lb/ton)
pH	within the range 6.0 to 9.0

Titanium Dioxide (Chloride and Sulfate Processes)

Although research is currently being conducted to determine the feasibility of acid recovery and recycle of process water, many problems remain unsolved. As such, it is not considered feasible to require this technology to be incorporated into new facilities. The new source performance standards for titanium dioxide require the same degree of effluent reduction attainable by the application of best available technology economically achievable, as presented in Section X. This technology is demonstrated and may be applied to new sources.

PRETREATMENT STANDARDS FOR NEW SOURCES

Plants whose waste water discharges are characterized by the presence of materials that interfere with operation of biological systems are not suited to use of conventional secondary waste treatment. Extreme segregation (that is, limiting the sewered discharge to sanitary and other organic wastes) or pretreatment is required by such manufacturing plants.

The pretreatment standards for new sources in the inorganic chemicals manufacturing category are the standards set forth in 40 CFR 128. In addition to these standards, however, the pretreatment standard for incompatible pollutants is the new source performance standard. If a publicly owned treatment works is committed to remove a specified percentage of any incompatible pollutant, the pretreatment standard is correspondingly reduced in stringency for that pollutant.

SECTION XII

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SECTION XIII

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SECTION XIV

GLOSSARY

Acidity

The total titratable hydrogen ion content of the solution is defined as the acidity. Acidity is expressed in mg/l of free hydrogen ion.

Adsorption

Condensation of the atoms, ions or molecules of a gas, liquid or dissolved substance on the surface of a solid called the adsorbent. The best known examples are gas/solid and liquid/solid systems.

Air Pollution

The presence in the air of one or more air contaminants in quantities injurious to human, plant, animal life, or property, or which unreasonably interferes with the comfortable enjoyment thereof.

Alkalinity

Total titratable hydroxyl ion concentration of a solution. In water analysis, alkalinity is expressed in mg/l (parts per million) of calcium carbonate.

Ash

The solid residue left after incineration in the presence of oxygen.

Bag Filter

A dry collection device for recovery of particulate matter from gas streams.

Barometric Condenser

Device, operating at barometric pressure, used to change vapor into liquid by cooling.

Blowdown

The minimum discharge of recirculating water for the purpose of discharging materials contained in the water, the further build-up of which would cause concentration in amounts exceeding limits established by best engineering practice.

Brine

An aqueous salt solution.

Calcination

The roasting or burning of any substance to bring about physical or chemical changes; e.g., the conversion of limestone to quicklime.

Carbonation

Treatment with carbon dioxide gas.

Catalytic Converter

A unit containing a packed or fluidized bed of catalyst.

Caustic

Capable of destroying or eating away by chemical action. Applied to strong bases and characterized by the presence of hydroxyl ions in solution.

Centrifuge

A device having a rotating container in which centrifugal force separates substances of differing densities.

Chemical Oxygen Demand, COD

Its determination provides a measure of the quantity of oxygen required to oxidize the organic matter (or other oxidizable matter) in a waste sample, under specific conditions of oxidizing agents, temperature and time. The general method is applied to waste samples having an organic carbon concentration greater than 15 mg/l.

Coke

The carbonaceous residue of the destructive distillation (carbonization) of coal or petroleum.

Conditioning

A physical and/or chemical treatment given to water used in the plant or discharged.

Conductivity, Electrical

The ability of a material to conduct a quantity of electricity transferred across a unit area, per unit potential gradient per unit time. In practical terms, it is used for approximating the salinity or total dissolved solids content of water.

Cooling Water

Water which is used to absorb waste heat generated in the process. Cooling water can be either contact or noncontact.

Copperas

Ferrous sulfate.

Cyclone Separator

A mechanical device which removes suspended solids from gas streams.

Demineralization

The removal from water of mineral contaminants usually present in ionized form. The methods used include ion-exchange techniques, flash distillation or electrolysis.

Electrostatic Precipitator

A gas cleaning device using the principle of placing an electrical charge on a solid particle which is then attracted to an oppositely-charged collector plate.

Filtrate

Liquid after passing through a filter.

Filtration

Removal of solid particles from liquid or particles from air or gas stream through a permeable membrane.

Flocculation

The combination of aggregation of suspended solid particles in such a way that they form small clumps. The term is used as a synonym for coagulation.

Fluidized Bed Reactor

A reactor in which finely divided solids are caused to behave like fluids due to their suspension in a moving gas or liquid stream.

Gas Washer (or Wet Scrubber)

Apparatus used to remove entrained solids and other substances from a gas stream.

Hardness (Total)

The characteristic of water generally accepted to represent the total concentration of calcium and magnesium ions, usually expressed as mg/l of calcium carbonate.

Heavy Metal

One of the metal elements not belonging to the alkali or alkaline earth group. In this study, the classification includes titanium, vanadium, iron, nickel, copper, mercury, lead, cadmium, and chromium.

Ion Exchange

A reversible chemical reaction between a solid and a fluid by means of which ions may be interchanged from one substance to another. The customary procedure is to pass the fluid through a bed of the solid, which is granular and porous and has a limited capacity for exchange. The process is essentially a batch type in which the ion exchanger, upon nearing depletion, is regenerated by inexpensive salts or acid.

Kiln (Rotary)

A large cylindrical mechanized type of furnace used for calcination.

Membrane

A thin sheet of synthetic polymer, through the apertures of which small molecules can pass, while larger ones are retained.

Mother liquor

The solution from which crystals are formed.

Multi-Effect Evaporator

In chemical processing installations, requiring a series of evaporations and condensations, the individual units are set up in series and the latent heat of vaporization from one unit is used to supply energy for the next. Such units are called "effects" in engineering parlance as, e.g., a triple effect evaporator.

Oleum or Fuming Sulfuric Acid

A solution of sulfur trioxide in sulfuric acid.

pH

Is a measure of the relative acidity or alkalinity of water. A pH value of 7.0 indicates a neutral condition; less than 7 indicates a predominance of acids, and greater than 7, a predominance of alkalis. There is a 10-fold increase (or decrease) from one pH unit level to the next, e.g., 10-fold increase in alkalinity from pH 8 to pH 9.

Plant Effluent or Discharge after Treatment

The waste water discharged from the industrial plant. In this definition, any waste treatment device (pond, trickling filter, etc.) is considered part of the industrial plant.

Pretreatment

The necessary processing given materials before they can be properly utilized in a process or treatment facility.

Process Effluent or Discharge

The volume of waste water emerging from a particular use in the plant.

Process Water

Water which is used in the internal plant streams from which products are ultimately recovered, or water which contacts either the raw materials or product at any time.

Reverse Osmosis

A method involving application of pressure to the surface of a saline solution forcing water from the solution to pass from the solution through a membrane which is too dense to permit passage of salt ions. Hollow nylon fibers or cellulose acetate sheets are used as membranes since their large surface areas offer more efficient separation.

Sedimentation

The falling or settling of solid particles in a liquid, as a sediment.

Settling Pond

A large shallow body of water into which industrial waste waters are discharged. Suspended solids settle from the waste waters due to the large retention time of water in the pond.

Sintering

The agglomeration of powders at temperatures below their melting points. Sintering increases strength and density of the powders.

Slaking

The process of reacting lime with water to yield a hydrated product.

Sludge

The settled mud from a thickener clarifier. Generally, almost any flocculated, settled mass.

Slurry

A watery suspension of solid materials.

Sniff Gas

The exhaust or tail gas effluent from the chlorine liquefaction and compression portion of a chlor-alkali facility.

Solute

A dissolved substance.

Solvent

A liquid used to dissolve materials.

Thickener

A device or system wherein the solid contents of slurries or suspensions are increased by evaporation of part of the liquid phase, or by gravity settling and mechanical separation of the phases.

Total Dissolved Solids (TDS)

The total amount of dissolved solid materials present in an aqueous solution.

Total Organic Carbon, TOC

A measurement of the total organic carbon content of surface waters, domestic and industrial wastes, and saline waters.

Total Suspended Solids (TSS)

Solid particulate matter found in waste water streams, which, in most cases, can be minimized by filtration or settling ponds.

Turbidity

A measure of the opacity or transparency of a sediment-containing waste stream. Usually expressed in Jackson units or Formazin units which are essentially equivalent in the range below 100 units.

Wet Scrubbing

A gas cleaning system using water or some suitable liquid to entrap particulate matter, fumes, and absorbable gases.

Waste Discharged

The amount (usually expressed as weight) of some residual substance which is suspended or dissolved in the plant effluent.

Waste Generated (Raw Waste)

The amount (usually expressed as weight) of some residual substance generated by a plant process or the plant as a whole. This quantity is measured before treatment.

Water Recirculation or Recycling

The volume of water already used for some purpose in the plant which is returned with or without treatment to be used again in the same or another process.

Water Use

The total volume of water applied to various uses in the plant. It is the sum of water recirculation and water withdrawal.

Water Withdrawal or Intake

The volume of fresh water removed from a surface or underground water source by plant facilities or obtained from some source external to the plant. The effluent limitations guidelines for sodium dichromate and byproduct sodium sulfate plants, based on the application of the best available technology economically achievable, require no discharge of process waste water pollutants to navigable waters. 9992;G

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